Organics Decomposition in Landfills and its Relation to Gas Production and Leachate Quality

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Introduction

- A landfill is a complex biological system
  - Aerobic biological reactions
  - Anaerobic biological reactions

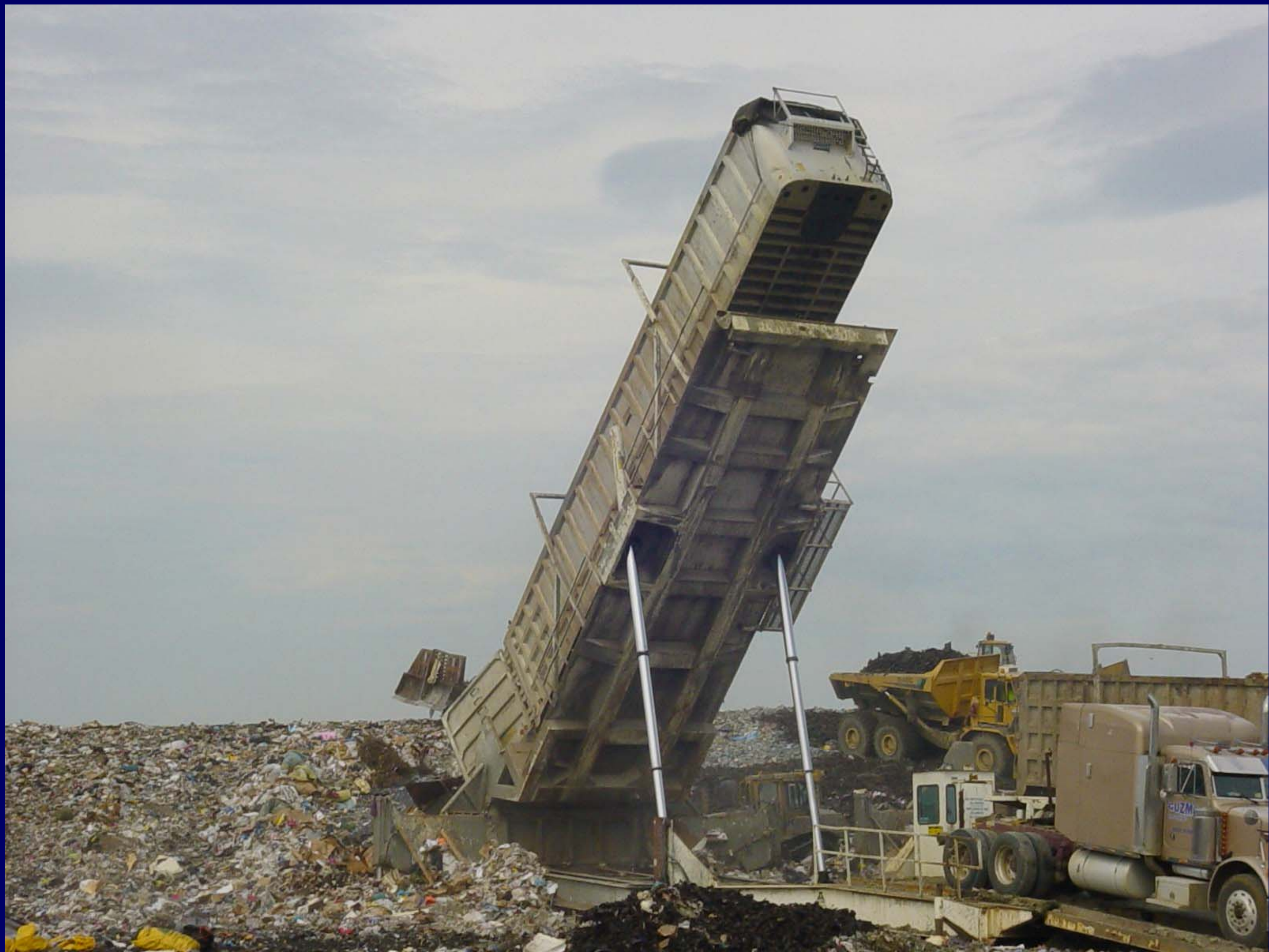
Introduction

- These reactions influence:
  - Gas production
  - Leachate production
  - Settlement
  - Final landfill status
- These reactions are influenced by:
  - Waste composition
  - Temperature
  - Moisture

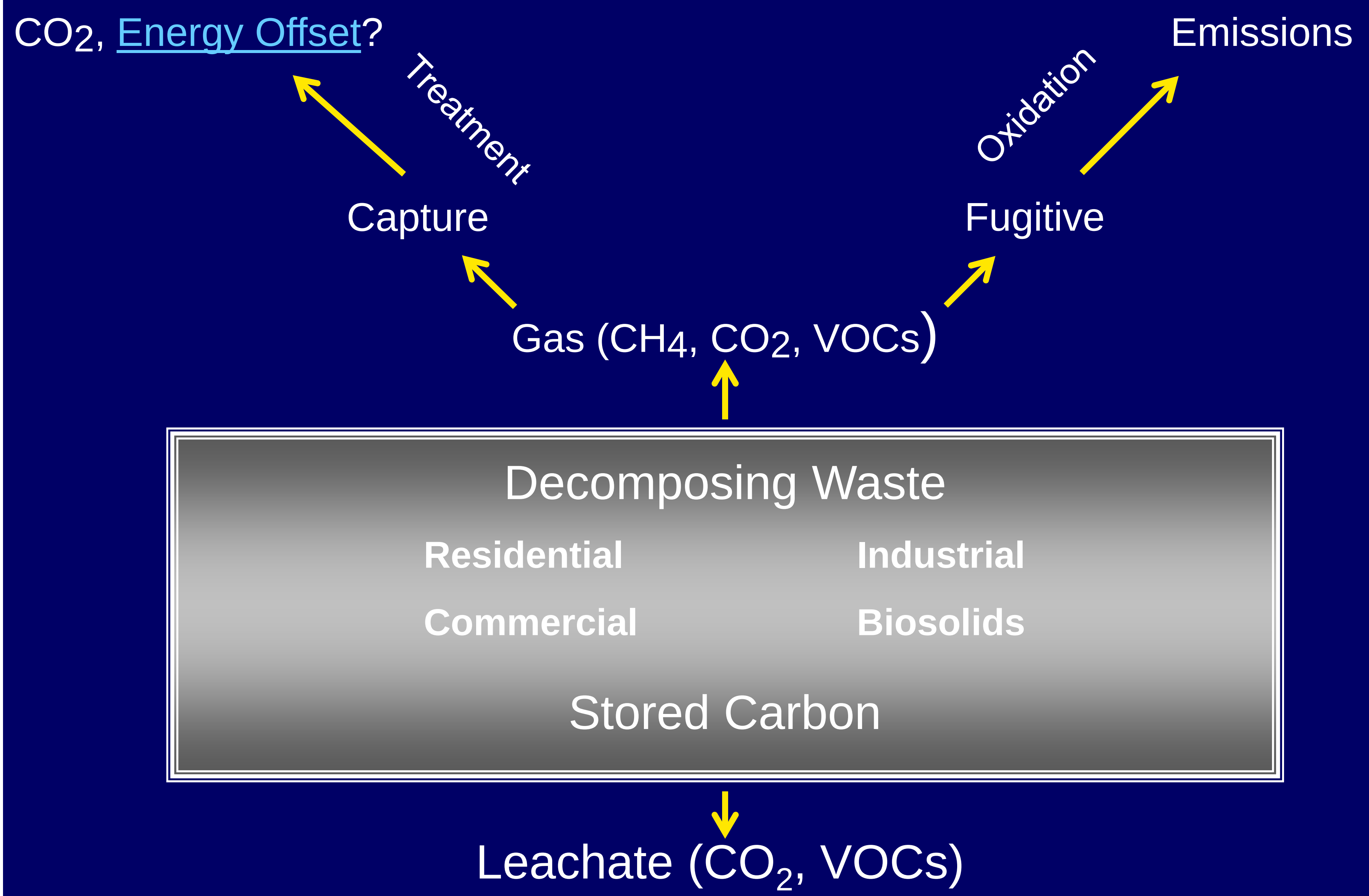
Objectives

- Develop an understanding of the biological conversion of municipal solid waste (MSW) to methane
  - The relationship between waste composition and gas generation
  - Gas generation and solids loss
  - Gas generation and leachate quality
  - Gas generation and gas collection

A Landfill Carbon Mass Balance



Carbon Flow In Landfills

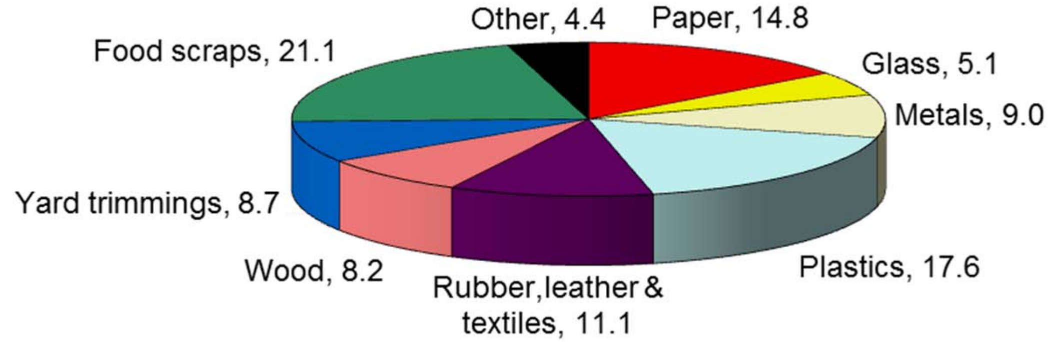


Biological Transformations of Refuse

- <u>Aerobic decomposition</u>
  - Organic matter + O_2 → CO_2 + H_2O + NH_3 + Heat
  - NH_3 + O_2 → NO_3
  - This is composting - air is supplied to refuse
    - occurs during storage and initial disposal

- <u>Anaerobic decomposition</u>
  - Organic matter ---> CO_2 + CH_4 + NH_3 + H_2S
  - Occurs in landfills
  - Methane is only produced in the absence of oxygen (O_2) which is not the same as H_2O

Municipal Solid Waste Composition Discarded Waste (2012)



US EPA 2014: Facts and Figures for 2012

Anaerobic Refuse Decomposition

Cellulose:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow 3n\ CO_2 + 3n\ CH_4$$

Hemicellulose:

$$(C_5H_8O_4)_n + nH_2O \rightarrow 2.5n\ CO_2 + 2.5n\ CH_4$$

Organic Composition of Residential Refuse (% Dry Wt.)

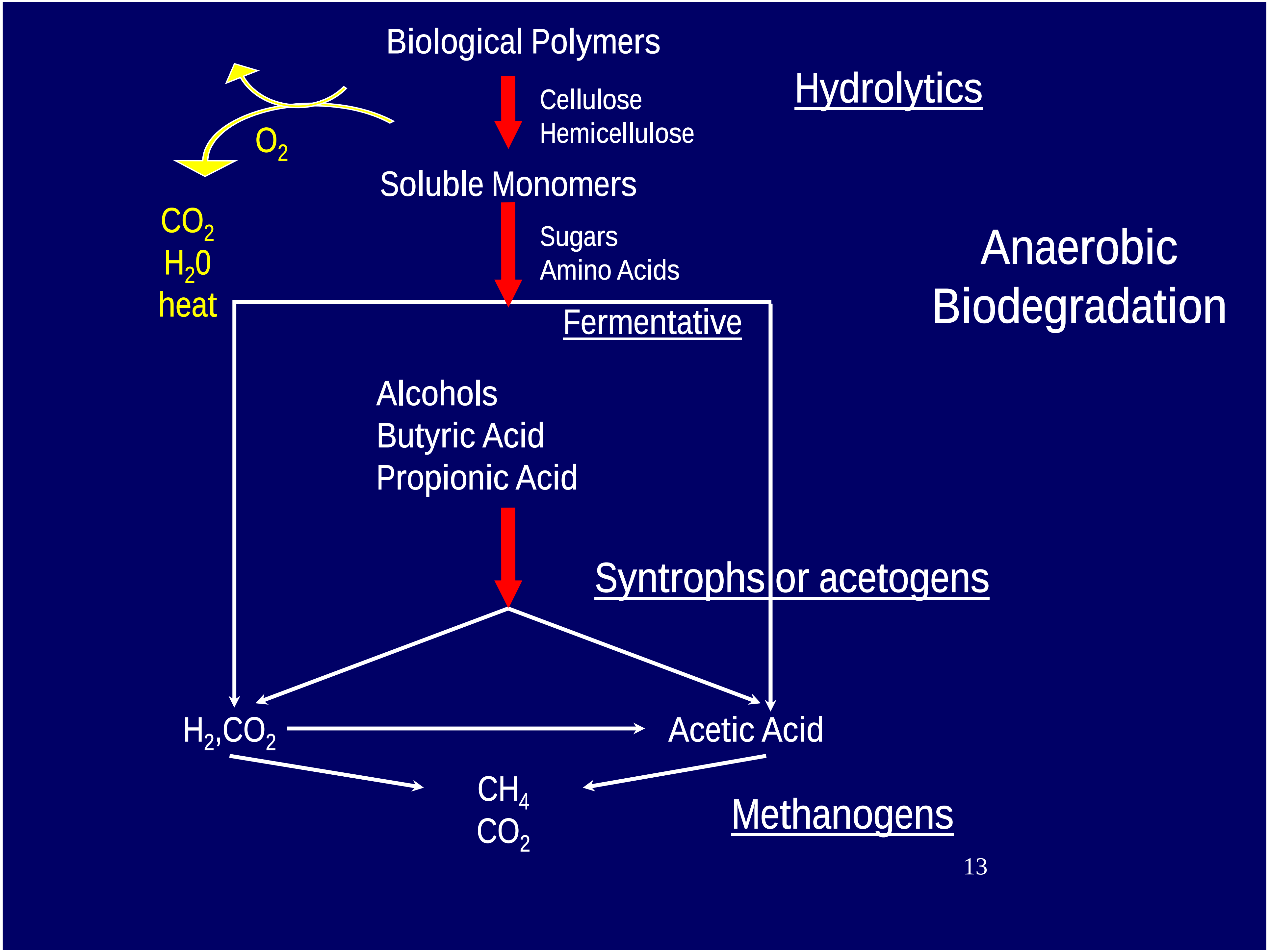
	News print	Copy Paper	OCC	Coated Paper	Branches	Grass	Leaves	Food Waste
Cellulose	44-48	58-65	57.3	35-42	27-40	26.5	15.3	18-33; 55 (incl. starch)
Hemi-cellulose	16.5-18	12.5	9.9	7.4-11.9	15-19	10.2	10.5	1; 7.2
Lignin	22-25	1.0	20.8	3.3-19.6	22-36	28.4	43.8	1.5; 11.4
Volatile solids	96-98	77-88	92.2	56-74	96-99	85	90.2	93.8

Organic Composition of Residential Refuse (% Dry Wt.)

	Fall	Winter	Spring	Summer	1985	Landfill
Cellulose	47	38.9	38.2	52.6	51.2	22.4
Hemi-cellulose	10.1	8.5	8.9	9.9	11.9	5.8
Lignin	19.6	31.2	30.1	12.8	15.2	11
Volatile solids	94	87.8	85.1	79.6		
CH/L	2.9	1.5	1.6	4.9	4.2	2.6

Where are we?

- Paper, yard waste and food waste are comprised of cellulose and hemicellulose
- These compounds are converted to CH_4 and CO_2 by bacteria under anaerobic conditions
- Several groups of bacteria are involved


Biological Polymers
Cellulose
Hemicellulose
Hydrolytics
O_2
Soluble Monomers
CO_2
H_20
heat
Sugars
Amino Acids
Anaerobic Biodegradation
Fermentative
Alcohols
Butyric Acid
Propionic Acid
Syntrophs or acetogens
H_2,CO_2
Acetic Acid
CH_4
CO_2
Methanogens

Refuse Decomposition

- Description of refuse decomposition in phases
  - Useful for understanding the status of a landfill and how decomposition occurs
  - Data measured in lab-scale landfills
  - The picture presented here applies to a small quantity of refuse undergoing uniform decomposition

1. Aerobic Phase

- Oxygen present when refuse is buried supports aerobic decomposition
- End products: H_2O, CO_2 - "CO_2 bloom"
- Waste heat of aerobic decomposition causes a temperature increase
- Carbon source is soluble sugars based on chemical composition

Aerobic Phase: Leachate Production And Quality

- Only useful if leachate represents a known area of refuse
- Limited volume in young landfills
- Strength may be high as water released from compacting refuse
- Refuse below field capacity
  - leachate due to preferential flow paths

2. Anaerobic Acid Phase (Commonly Referred to as Acid Phase)

- All oxygen consumed, no significant mechanism for replenishment
- Carboxylic acids accumulate due to an imbalance in microbial activity:
  - Butyrate $CH_3CH_2CH_2COOH$
  - Propionate CH_3CH_2COOH
  - Acetate CH_3COOH
- High CO_2 concentrations
- CH_4 just detected
- May be some H_2

2. Anaerobic Acid Phase Leachate Quality

- High COD, BOD (70% - 90% is acids)
- COD: chemical oxygen demand
  - Mass of oxygen to convert organics to CO_2 via a strong chemical reaction
- BOD: biochemical oxygen demand
  - Mass of oxygen to convert organics to CO_2 biologically
- BOD/COD changes during decomposition

2. Anaerobic Acid Phase Leachate Quality

- High COD, BOD (70% - 90% is acids)
- Low pH
- High metal dissolution
- Some solids (cellulose, hemicellulose) hydrolysis
- The acid phase explains the lag between burial and methane production in landfills
- May not be observed in an older landfill producing methane

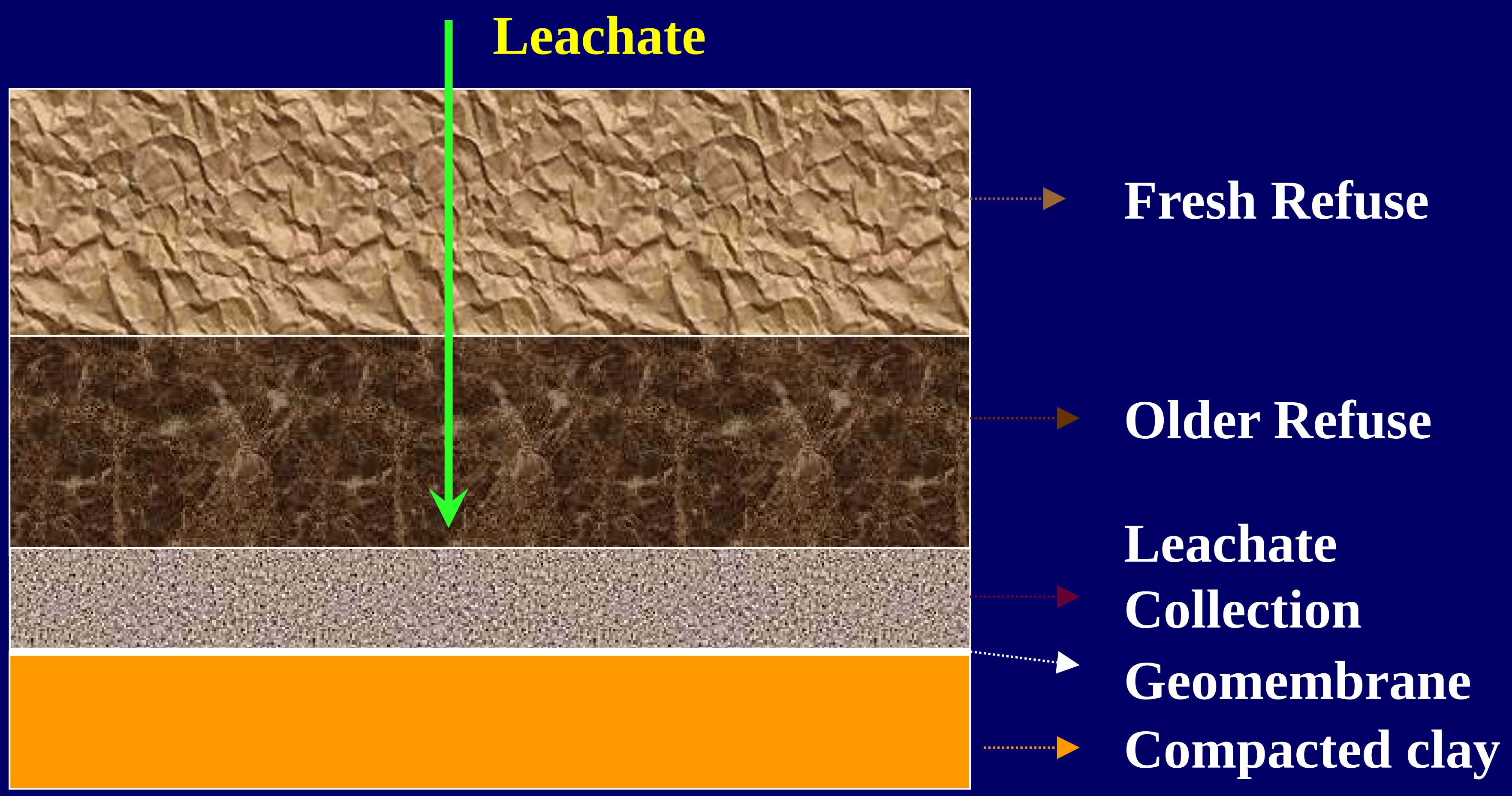
3. "Accelerated" Methane Production Phase

- Rapid increase in methane production rate
  - Typical concentration 50% - 70% CH_4
- Carboxylic acid concentrations decrease, pH increases to 7 - 8
- Activity of the three groups of bacteria is balanced
- The sharp increase and decrease presented in the figure are dampened in full-scale landfills
- Many combine phases 3 and 4

Phase 3: Leachate Quality

- Similar to acid phase depending on landfill
- May not be observed if this leachate flows through well decomposed waste below prior to collection

Leachate Quality Interpretation



4. "Decelerated" Methane Production Phase

- Carboxylic acids (soluble substrate) are depleted
- Rate of CH_4 production is dependent upon solids hydrolysis
- Activity of the three groups of bacteria is balanced
- Gas composition constant
- Leachate quality
  - COD is significantly lower
  - Acids are a much lower fraction of COD
  - Humic materials representative of very mature refuse are present

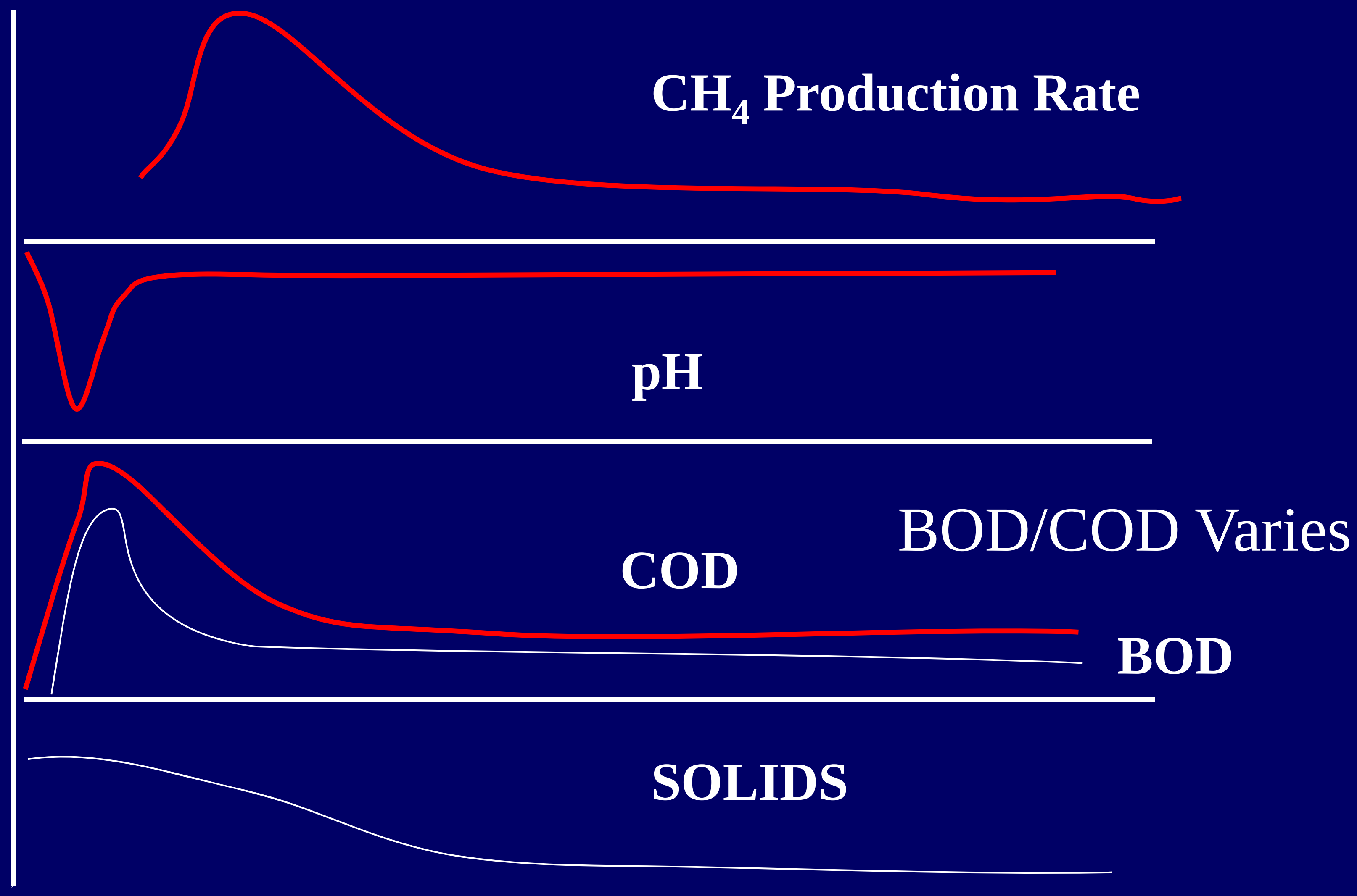
5. Complete Stabilization (Theoretical)

– Degradable solids completely consumed

– O_2 infiltrates the landfill and is not consumed

– May only occur over geologic time

Trends in Methane, COD, and pH



Refuse Decomposition

- Refuse decomposition is affected by:
  - Climate, surface hydrology, pH, temperature, operations
- Exerts an influence on:
  - Gas composition and volume
  - Leachate composition

Refuse Moisture Content

- Spatial Heterogeneity
  - Food waste and copy paper in Seattle and New Mexico is similar in moisture content
    - Moisture in landfill may be localized in the absence of infiltration

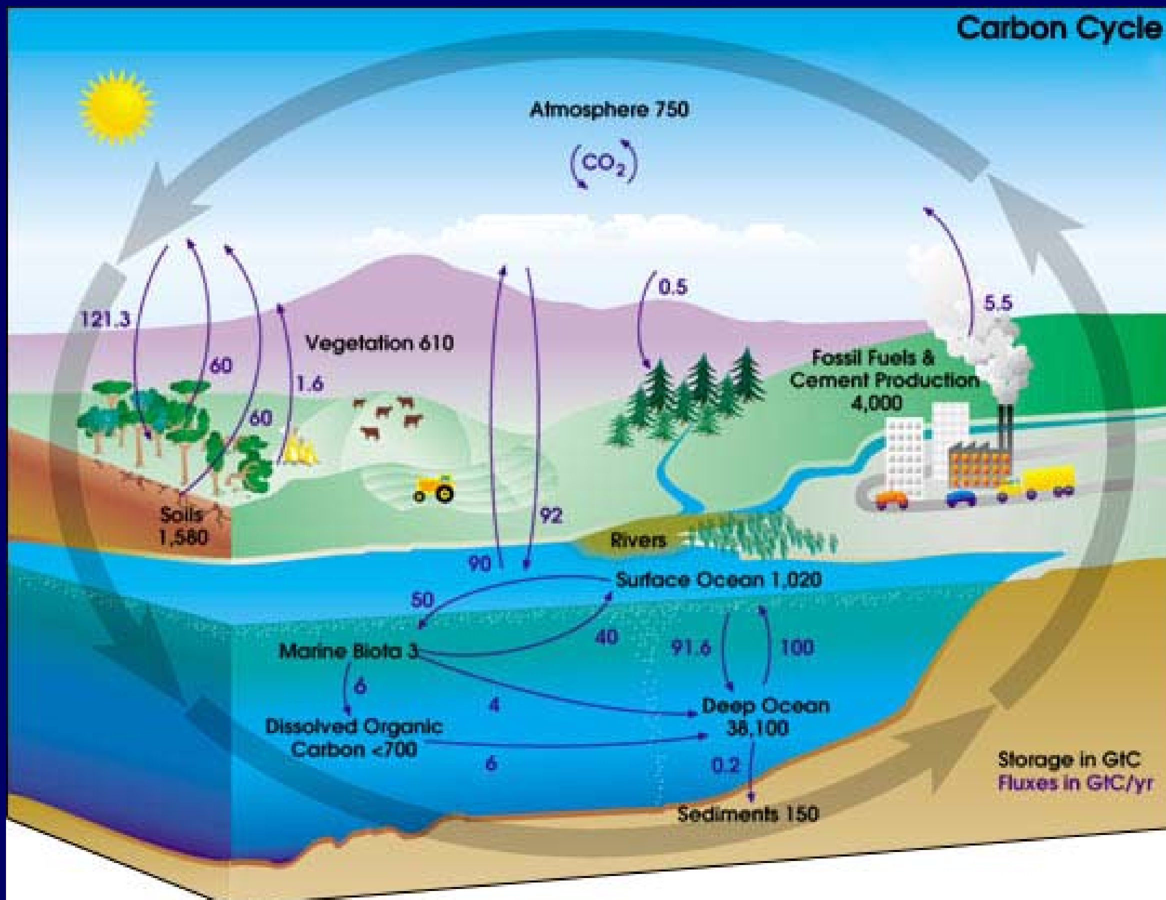
Waste Diversion

- Programs are increasingly accepting mixed fiber
  - Long-term methane potential
- Food waste diversion
  - Less effect on landfill methane due to rapid decay rate relative to collection schedule

Solids Decomposition and Carbon Storage

- Information on carbon storage and waste biodegradability are required to:
  - Evaluate how storage and methane yields change with refuse composition
  - Estimate national methane emission inventories and attribution of carbon sequestration credits

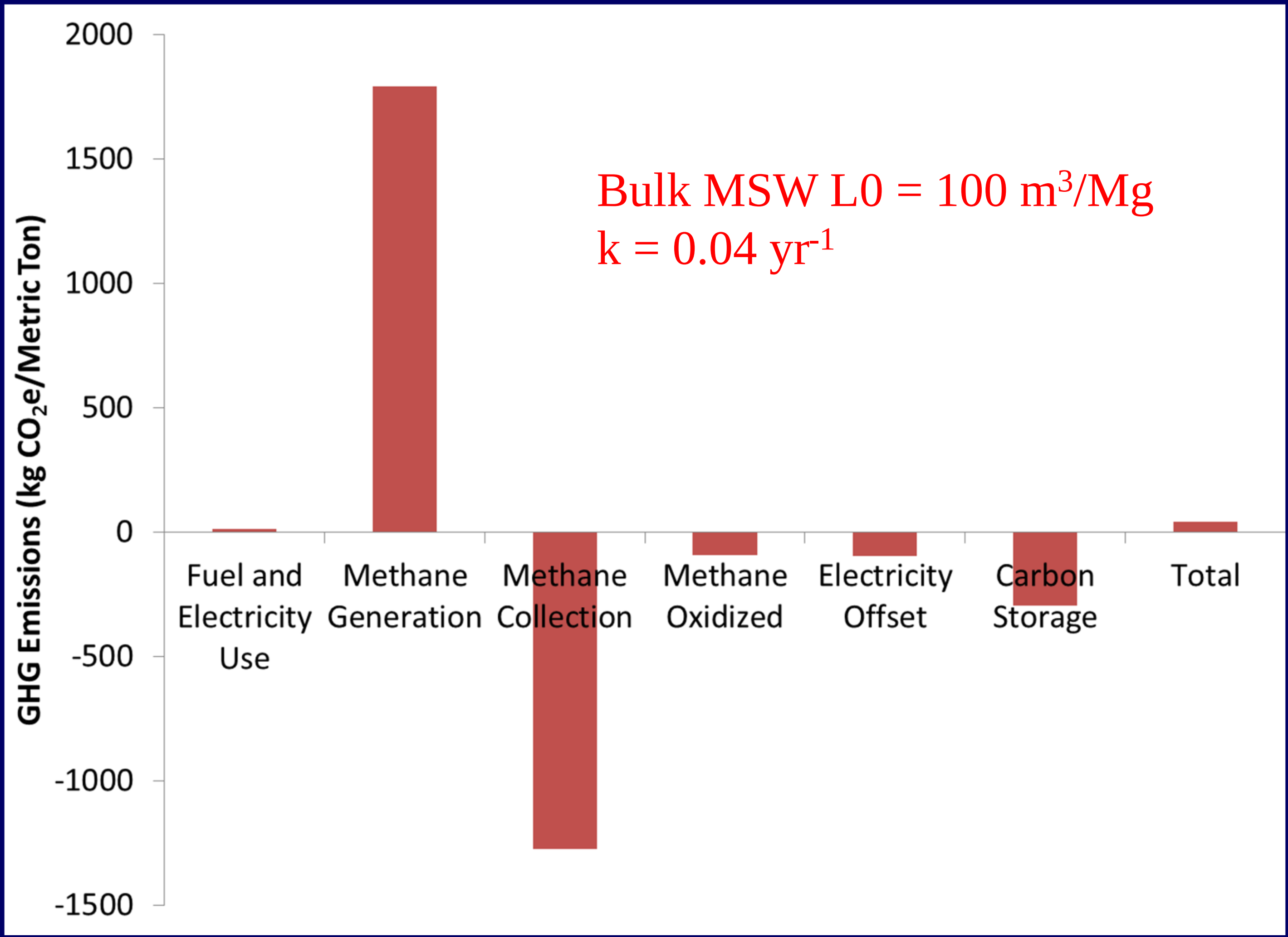
Lets Begin with the Carbon Cycle



CO_2 is removed from the atmosphere to grow forest products (paper, wood) and agricultural products. When these products decay, the CO_2 is returned to the atmosphere. If these products do not decay, then the carbon is considered to have been sequestered.

http://earthobservatory.nasa.gov/Library/CarbonCycle/Images/carbon_cycle_diagram.jpg

Importance of Carbon Storage

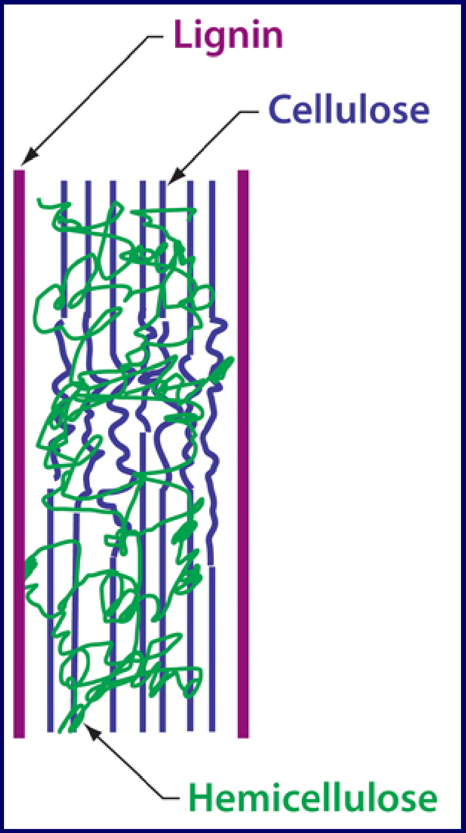


Carbon Sequestration in Landfills

- Food discards, yard trimmings, and paper are not completely decomposed by anaerobic bacteria; some of the carbon in these materials is stored in a landfill.
- Because this carbon storage would not normally occur under natural conditions (virtually all of the organic material would degrade to CO_2, completing the photosynthesis/respiration cycle), this is counted as an anthropogenic sink.
- Carbon in plastic that remains in the landfill is not counted as stored carbon, because it is of fossil origin.

The Role of Lignin

- Physically impedes microbial access to cellulose and hemicellulose
- Largely recalcitrant
  - Slight modifications to side chains but no demonstrated weight loss
    - 2 - 4% of natural pine lignin converted to CH_4 and CO_2



www.ligninbiofuels.com

Not all Lignins are Equal

- Softwood lignin
- Hardwood lignin
- Grass lignin
  - Relatively heavily lignified grass degraded to a larger extent than forest products

Carbon Sequestration in Landfills

- Lignin undergoes chemical and microbial transformation to humic matter which is another form of carbon storage
- Some cellulose and hemicellulose is not bioavailable because of lignin

Humic Matter

- Complex and heterogeneous mixtures of materials
  - formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains (a process called humification)
  - Plant lignin and its transformation products are important components taking part in this process.

Solids Decomposition

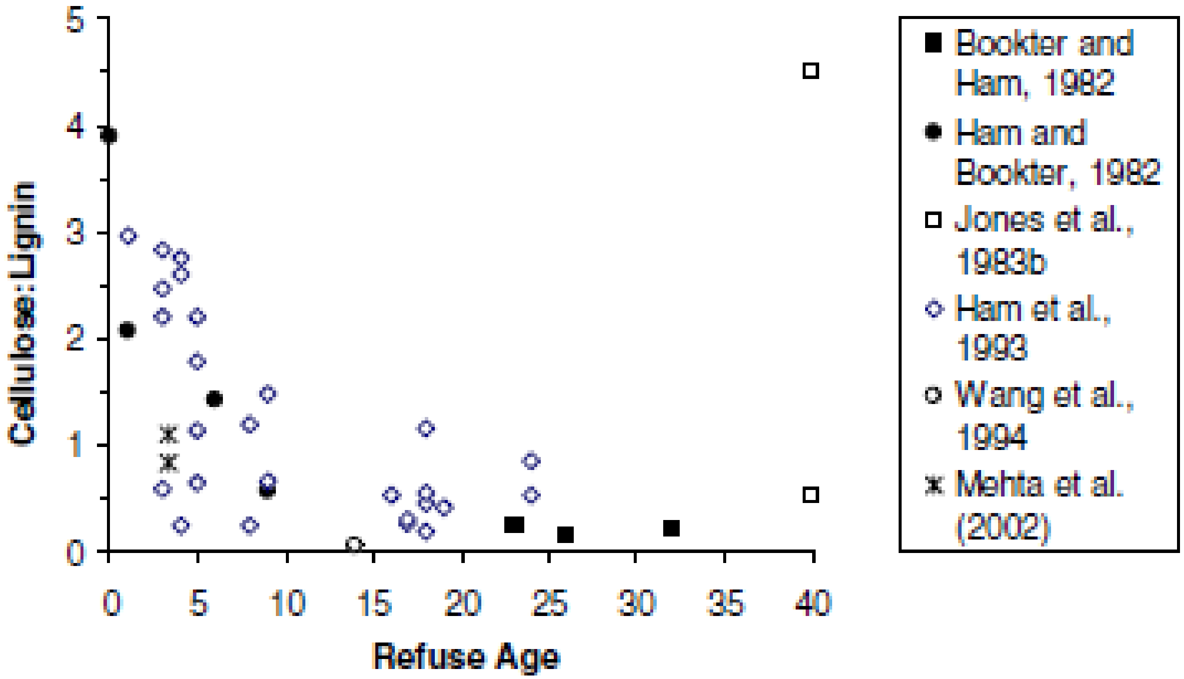


Fig. 1. Cellulose to lignin ratio for excavated samples. The data for Jones et al. (1983b) represent samples above (4.5) and below (0.54) the water table. The sample age is unknown and is plotted at year 40 for illustration only. For Wang et al., the average C/L for the 11 samples reported in Table 8 is plotted at the average age (14 years) as the sample age is not known. Average C/L data are also plotted for Mehta et al. (2002). The lower value is for refuse excavated from a test cell operated with leachate recirculation as described in the text.

Solids Decomposition

Table 6

Chemical composition and BMP of samples excavated from North Waterfront Park landfill (Wang et al., 1994)

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	CH:L[a]	C:L[a]	BMP (mL CH_4/dry gm)
1	0.9	0.5	85.6	0.016	0.011	1.0
2	4.5	1.5	73.2	0.082	0.061	9.1
3	3.8	1.9	76.9	0.074	0.049	3.2
4	1.9	0.8	77.2	0.035	0.025	2.5
5	11.7	2.5	70.9	0.2	0.165	30.7
6	5.4	1.8	75.3	0.096	0.072	9.1
7	1.5	0.6	84.5	0.025	0.018	1.0
8	1.0	0.4	85.2	0.016	0.012	0
9	5.7	2.5	72.1	0.113	0.079	0
10	4.6	1.7	68.2	0.092	0.067	1.6
11	1.0	0.5	72.0	0.21	0.014	Not measured

[a] The ratio of cellulose plus hemicellulose to lignin (CH:L) or cellulose to lignin (C:L).

Where are we?

- Paper, yard waste and food waste are comprised of cellulose and hemicellulose
- These compounds are partially converted to CH_4 and CO_2 by bacteria under anaerobic conditions, and partially preserved
- Lignin is largely recalcitrant and blocks some cellulose and hemicellulose
- Some lignin is transformed to humic matter

Stoichiometric Methods for Estimation of Methane Potential

1. General stoichiometric formula which includes all organics
   – some organics do not degrade

2. Estimate from methane potential of refuse

$$C_nH_aO_bN_c + (n - a/4 - b/2 + 3c/4)H_2O \text{ ----> } (n/2 - a/8 + b/4 + 3c/8)\ CO_2 + (n/2 + a/8 - b/4 - 3c/8)\ CH_4$$

Methane potential of remaining refuse: Biochemical Methane Potential (BMP) Test

- Measure maximum attainable methane production
- Sample is ground to a powder
- Incubated for 60 days in culture medium with an inoculum of microbes acclimated to refuse
- Methane production is measured
- Representative sampling still an issue
- Research tool/not practice

Methane Production From Landfills

- Landfill gas = $CH_4 + CO_2$
- Methane production rate = CH_4

Methane Production From Landfills

- Composition under steady methane production

CH_4	50 - 70%
CO_2	30 - 50
N_2	2 – 5
O_2	0.1- 1
H_2	0 0- 0.2
CO	0 - 0.02
Trace*	0.01 - 0.6

Air is 79/21
Over pumping vs. above ground leaks

** petroleum hydrocarbons, chlorinated aliphatics, alkanes, ketones, aldehydes, alcohols, terpenes, siloxanes, H_2S*

- Pumping scenario will influence oxygen and nitrogen content significantly

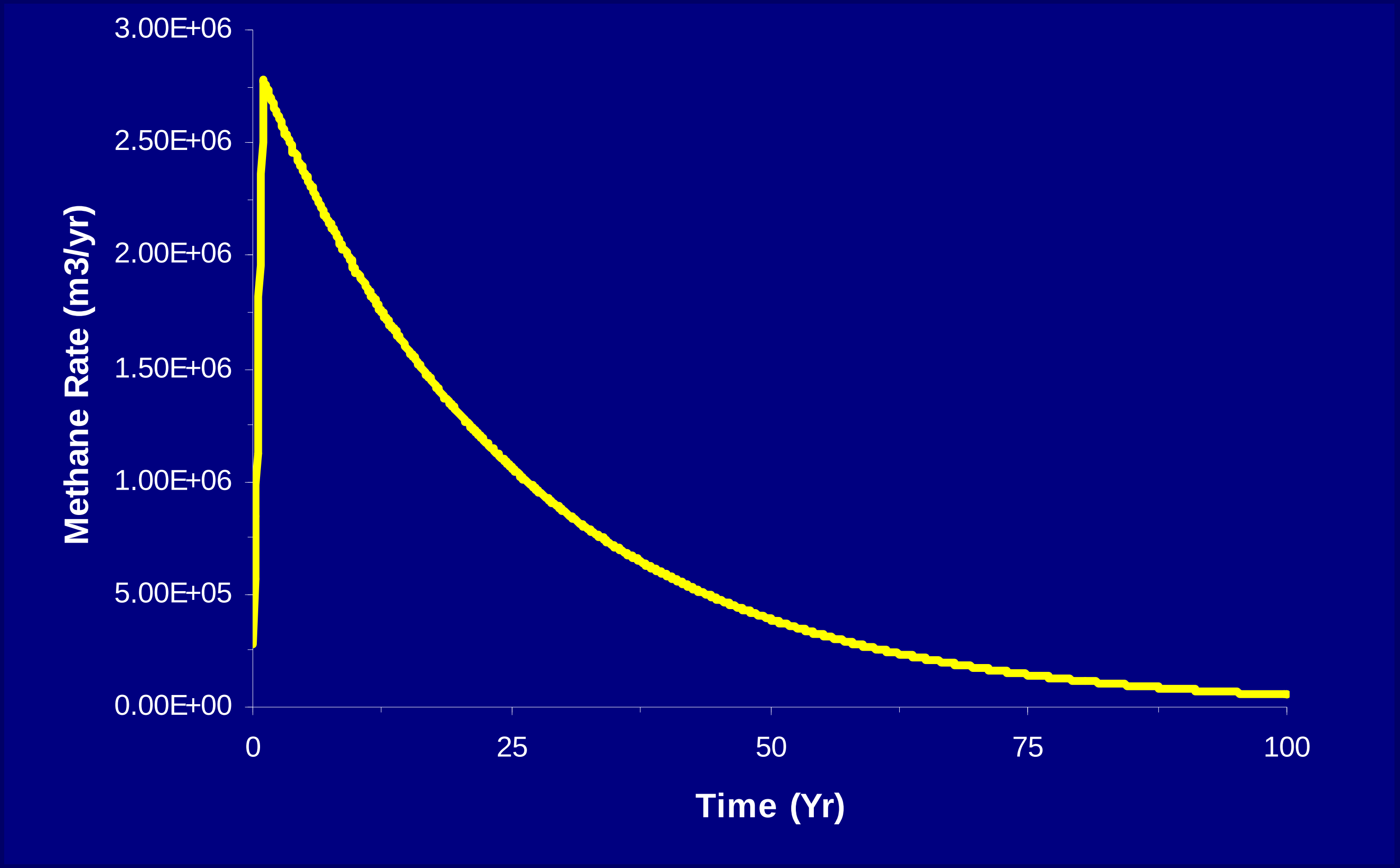
Landfill Gas Modeling

$$Q_n = k \cdot L_0 \cdot \sum_{i=0}^{n} \sum_{j=0.0}^{0.9} \frac{M_i}{10} \cdot e^{-k \cdot t_{i,j}}$$

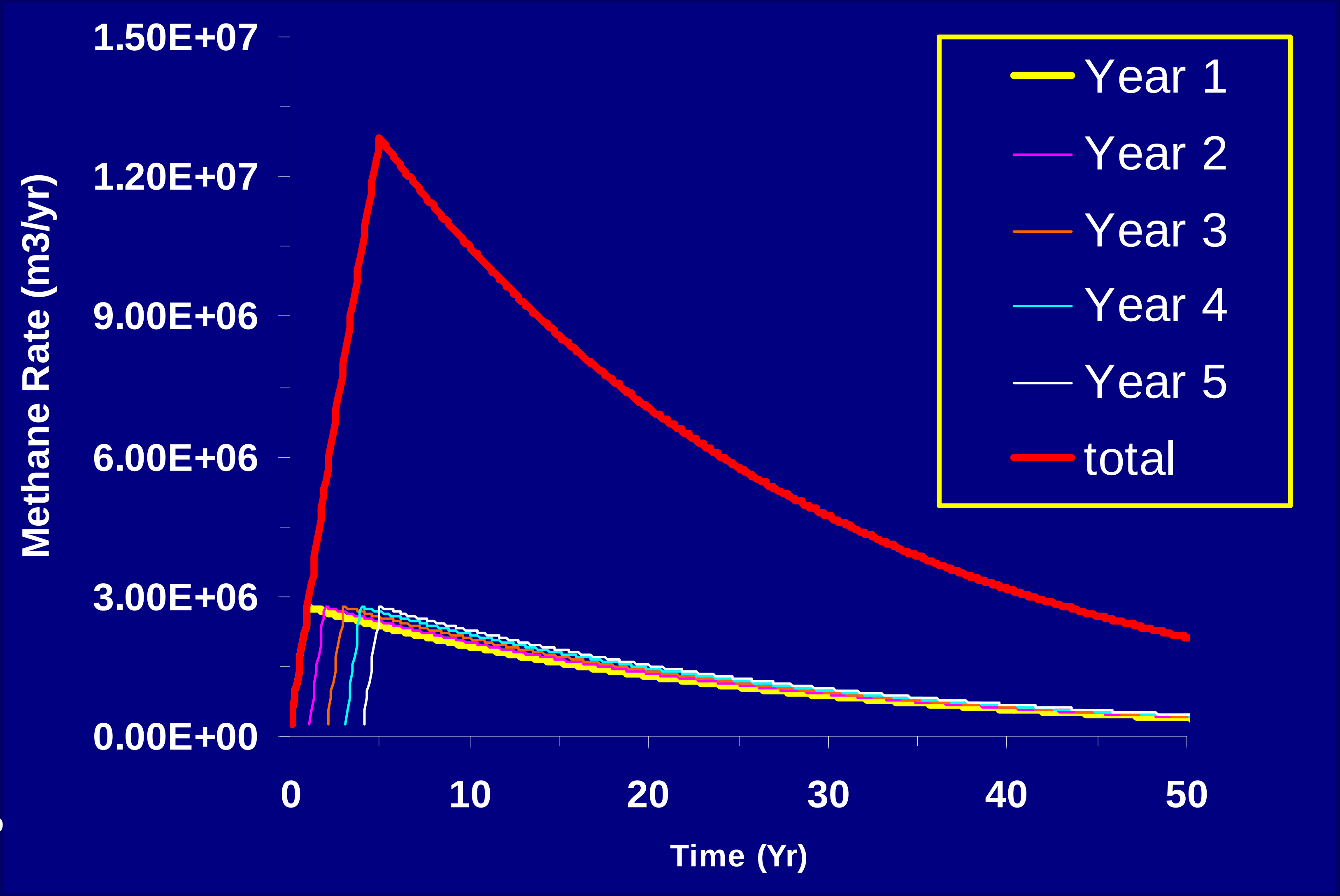
- **Q_n** is annual methane generation for a specific year t (m^3 CH_4/yr);
- **k** is first order decay rate constant (1/yr)
- **L_0** is total methane potential (m^3 CH_4/ton of waste);
- **M_i** is the annual burial rate (wet tons)
- **t** is time after initial waste placement (yr);
- **j** is the deci-year time increment

Landfill Gas Emissions Model (LandGem)
http://www.epa.gov/ttn/catc/products.html#software

Methane Production Rate Curve for One Year of Waste



Methane Production Rate Curve for Five Years Waste



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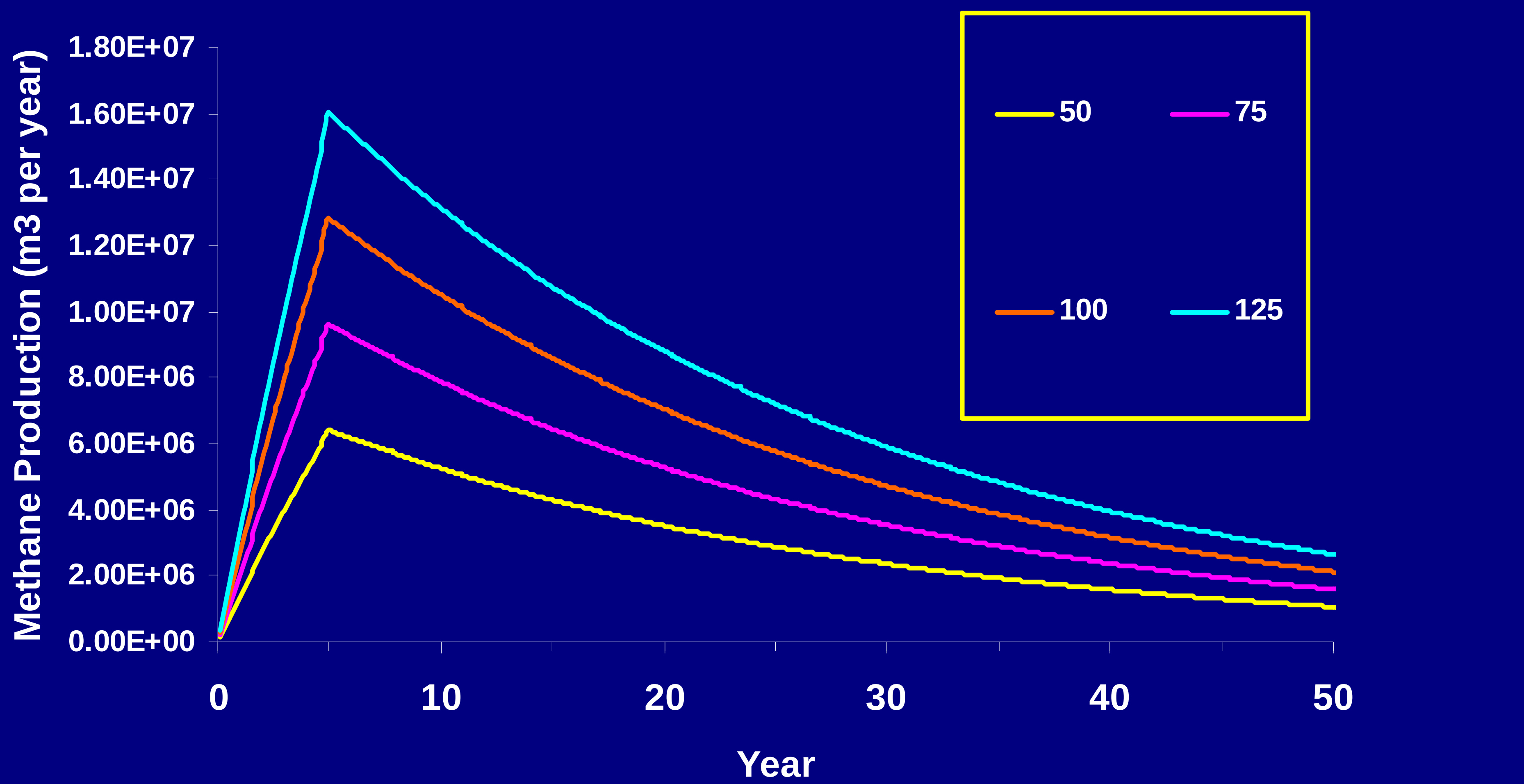
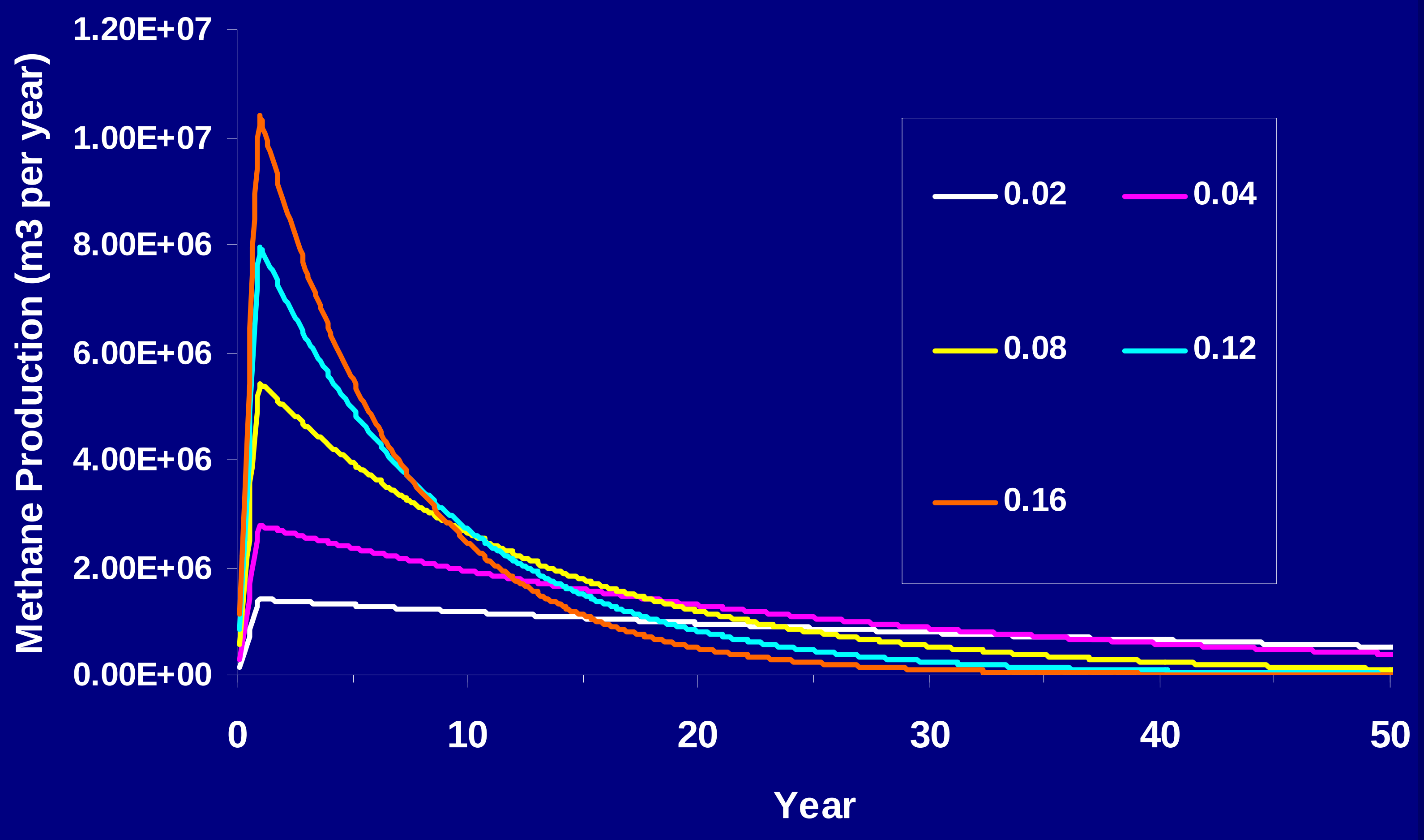
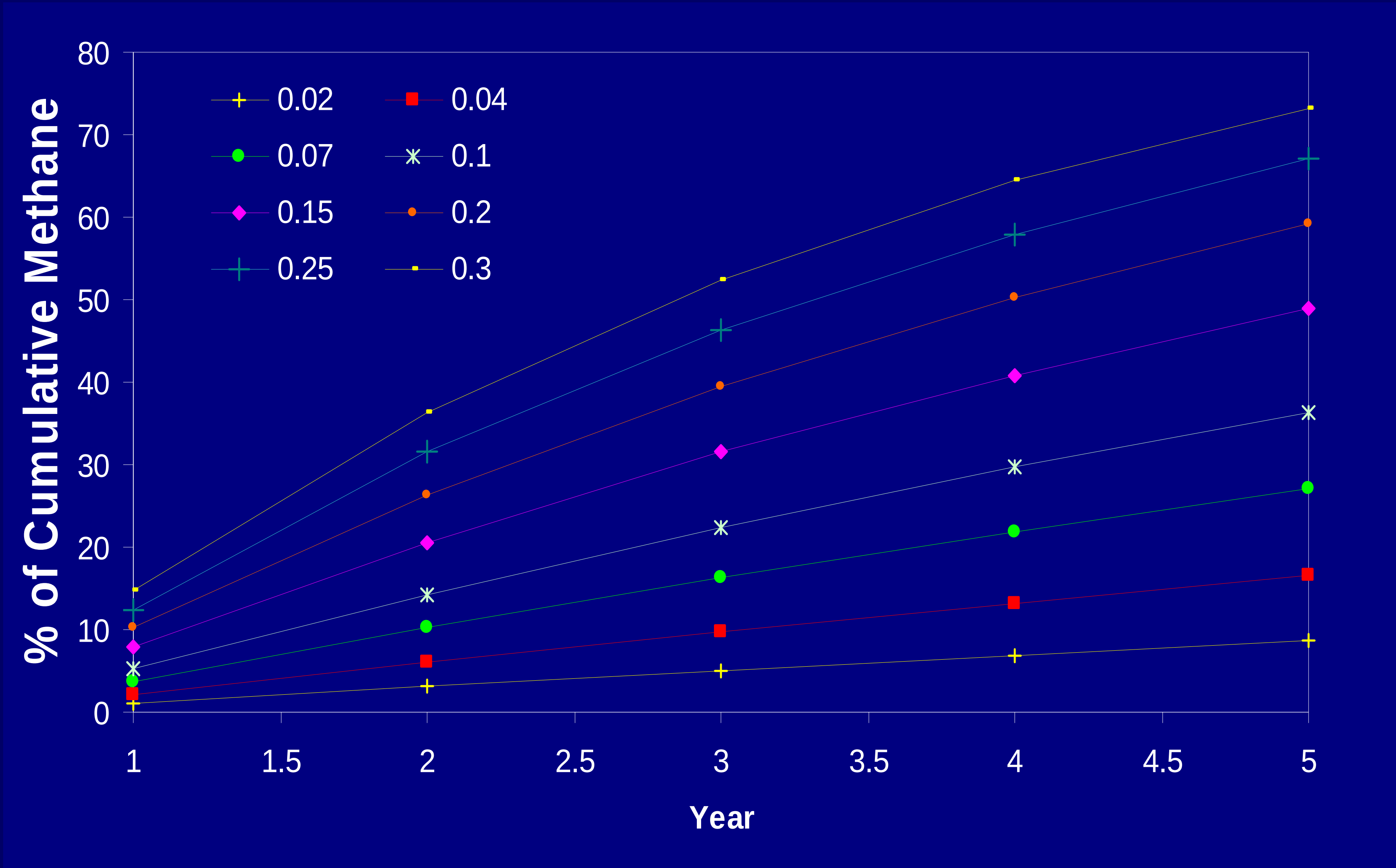
Effect of L_0 on Methane Production



Effect of Decay Rate (k) on Methane Production



Effect of Decay Rate (k) on Methane Production

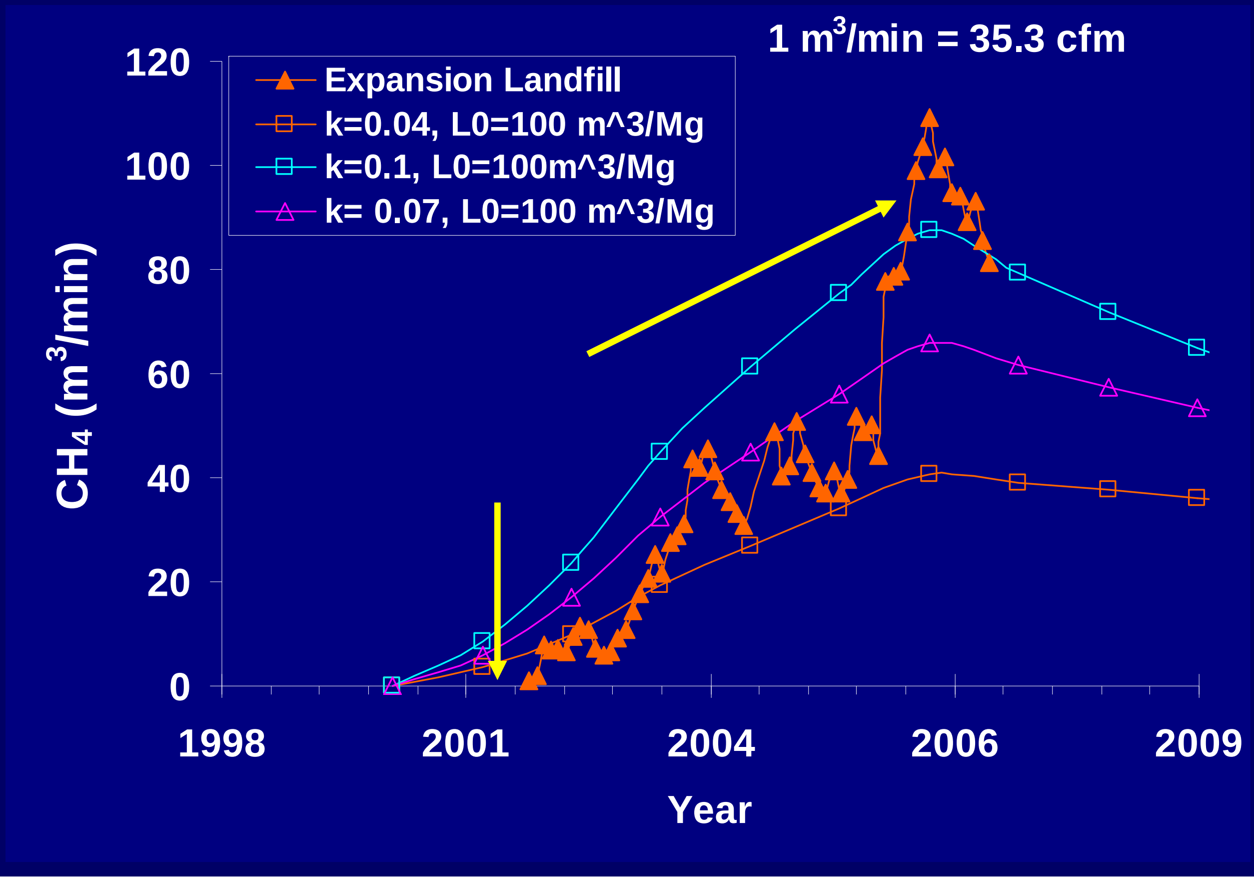


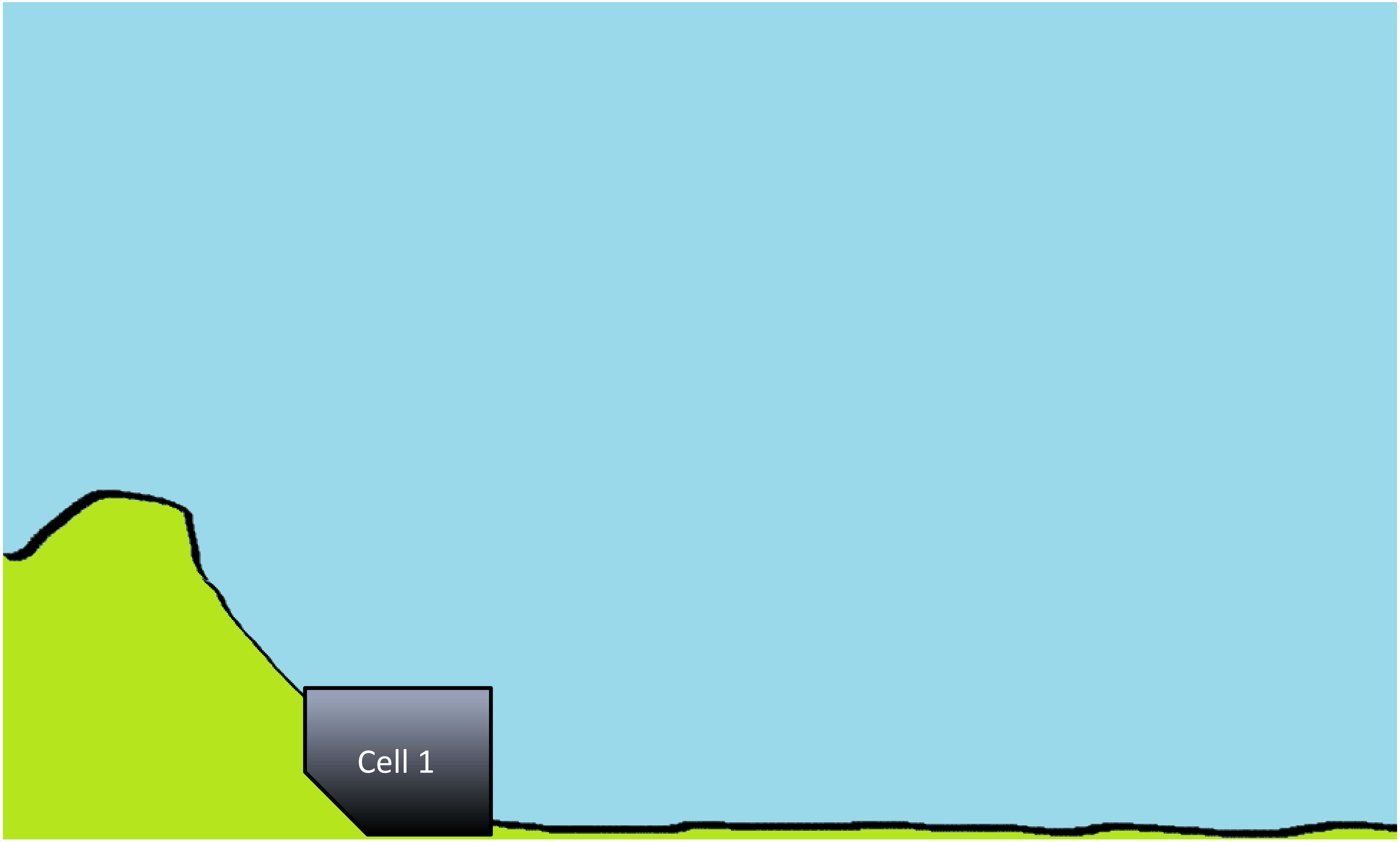
Landfill Gas Modeling

- Difference between production and collection
- Decay rate will vary dependent upon climate and operating conditions
- Simple model with only two variables (k, L_0)
  - Moisture and temperature are rolled into k
- Difficult to parameterize a more complex model

Collection Efficiency

- Collection efficiency varies with time
- Use of a temporally averaged value

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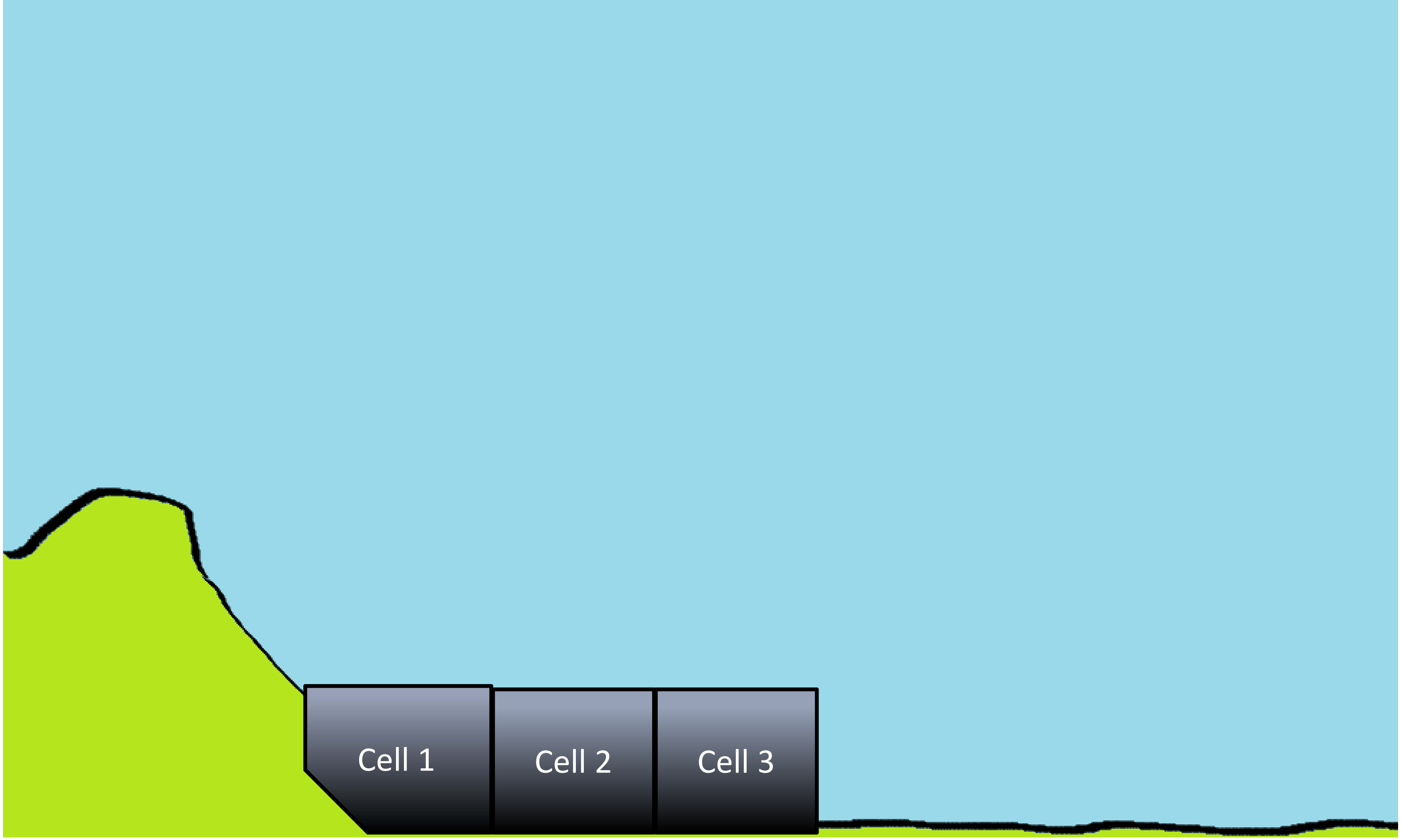
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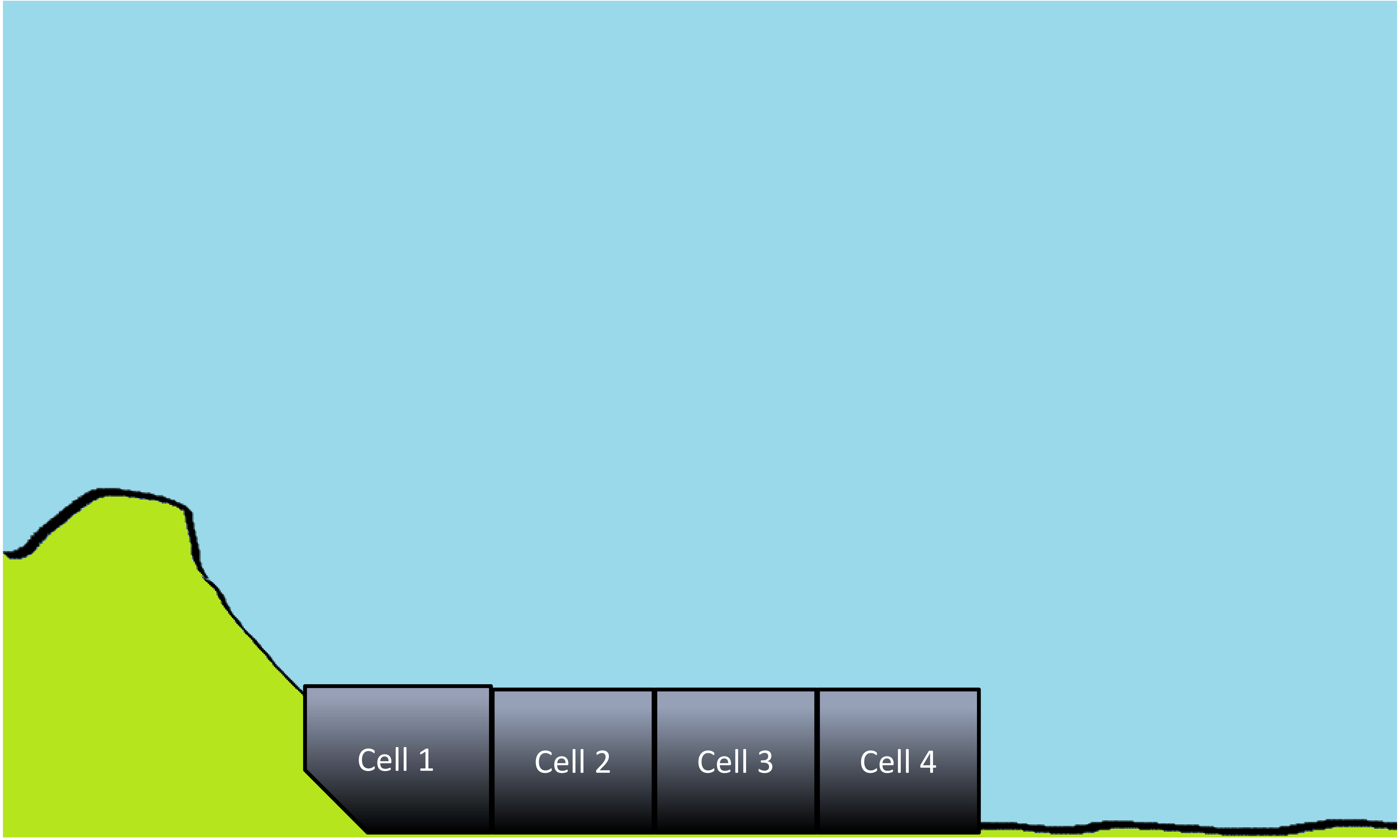
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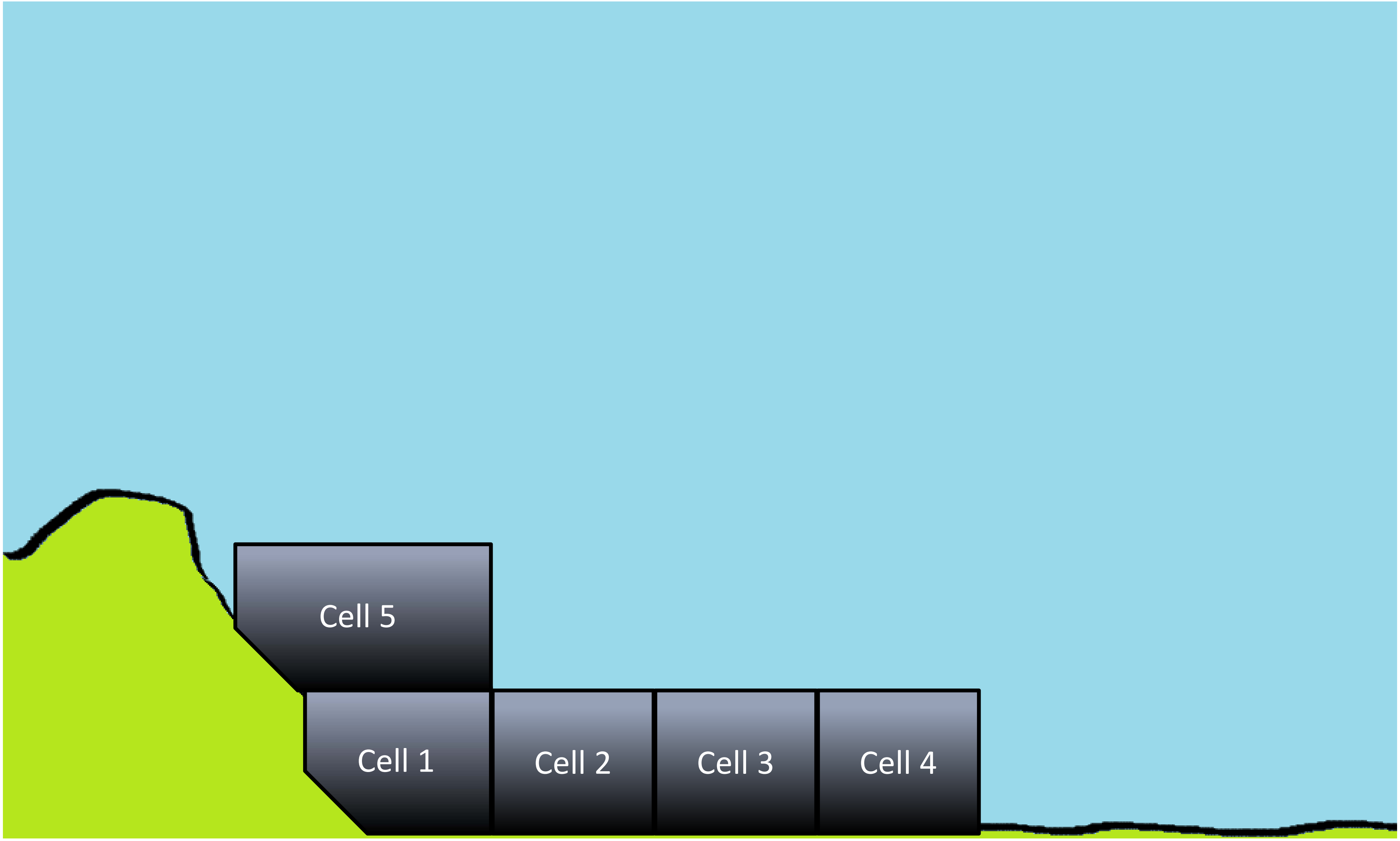
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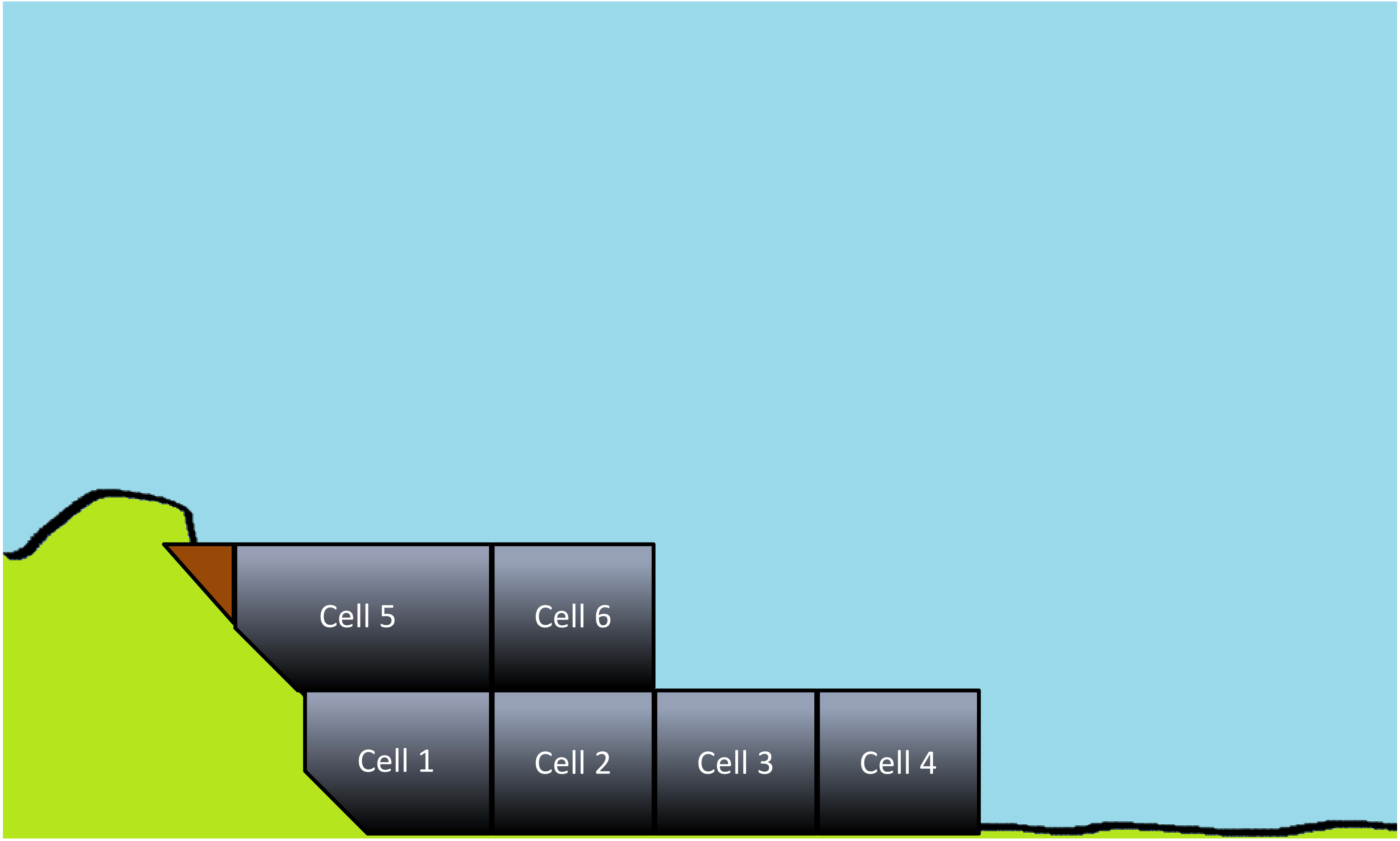

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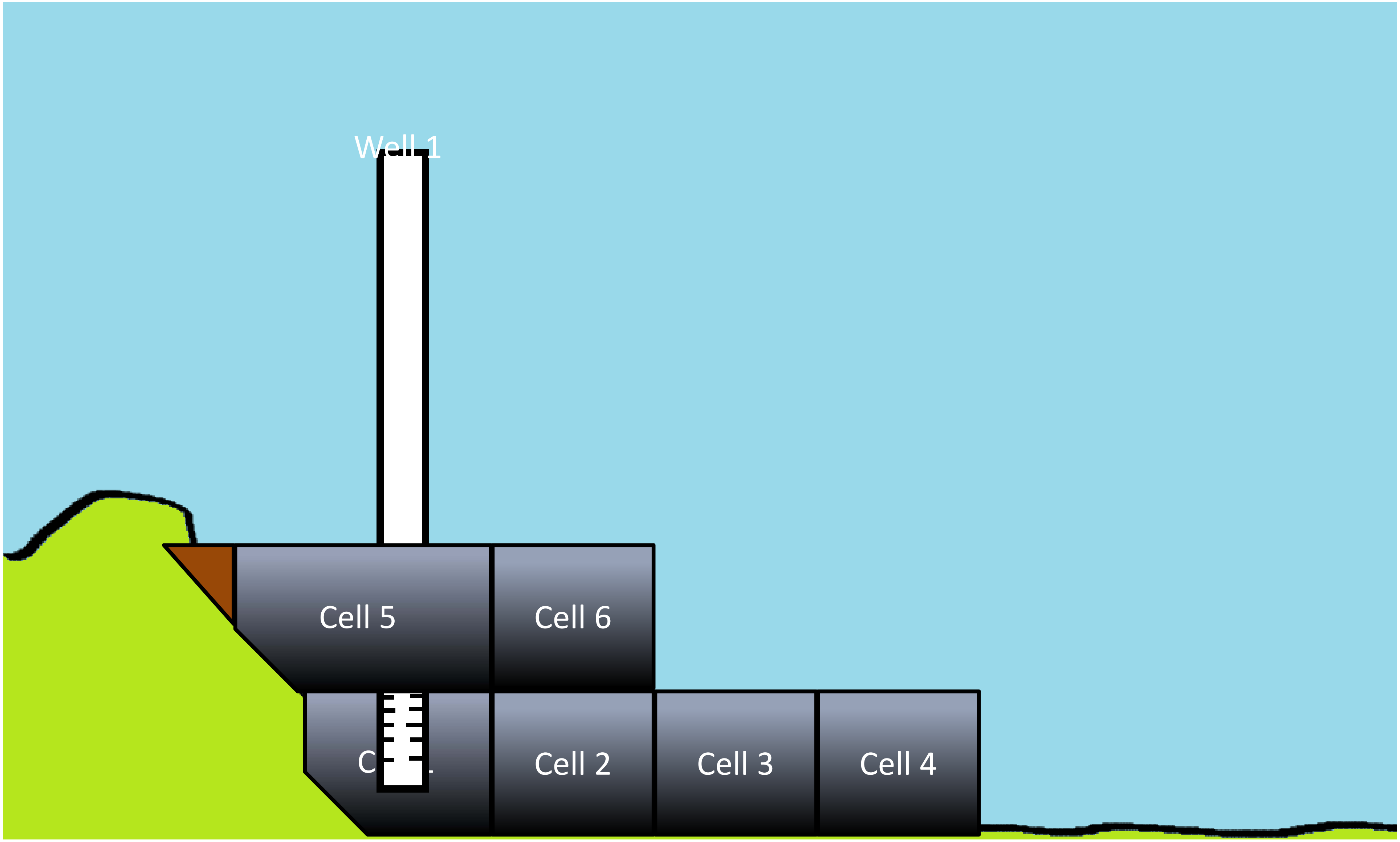
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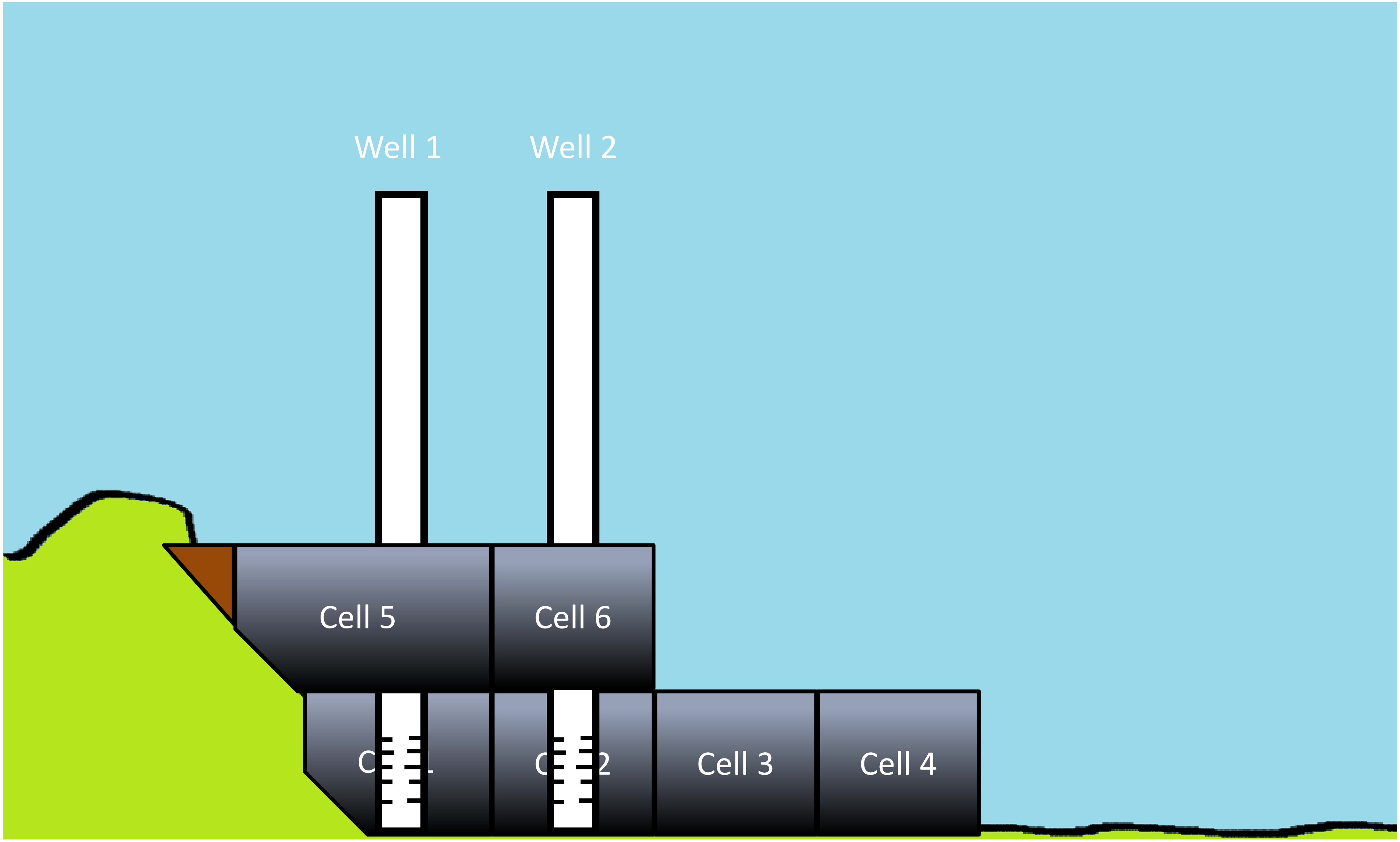
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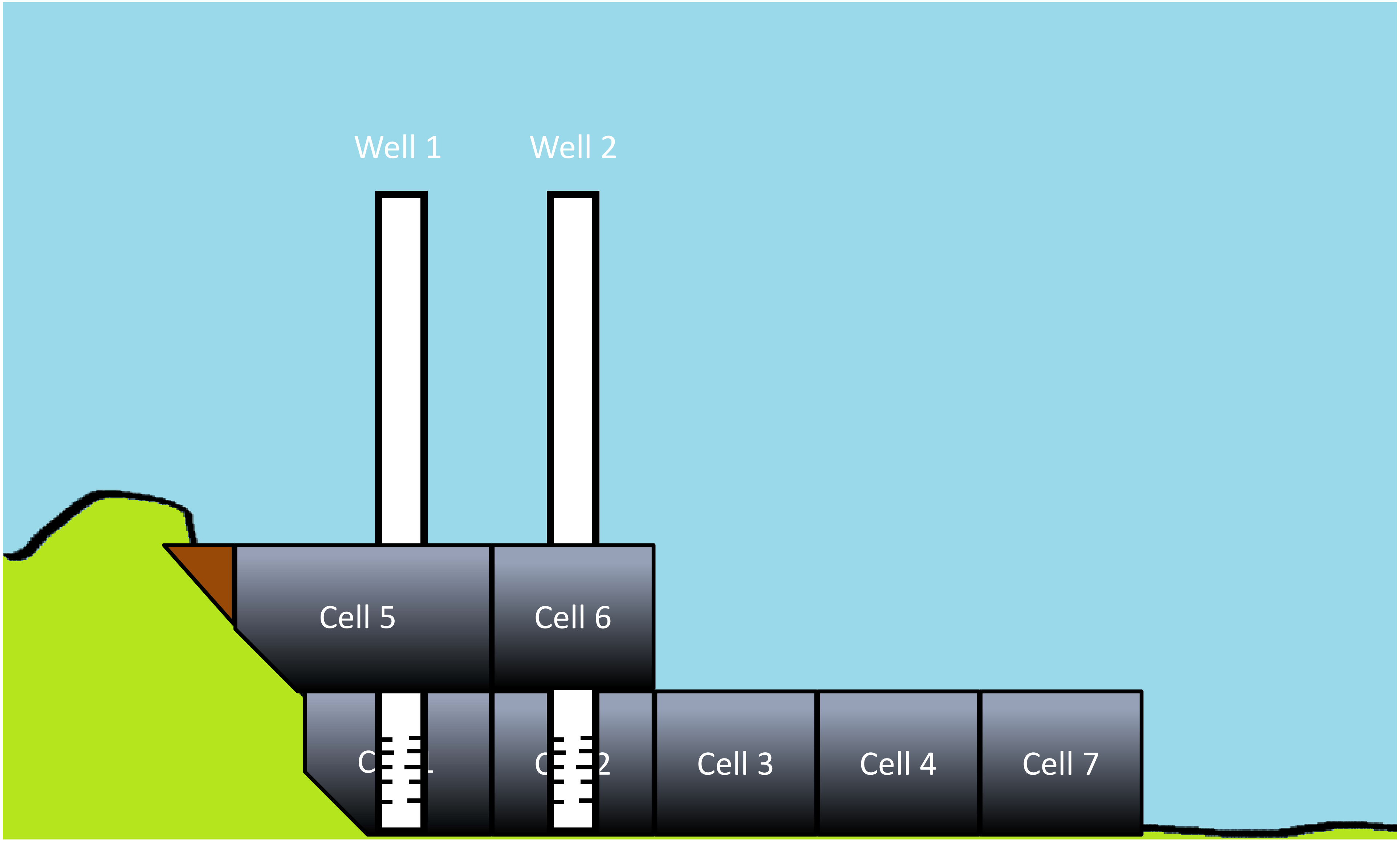
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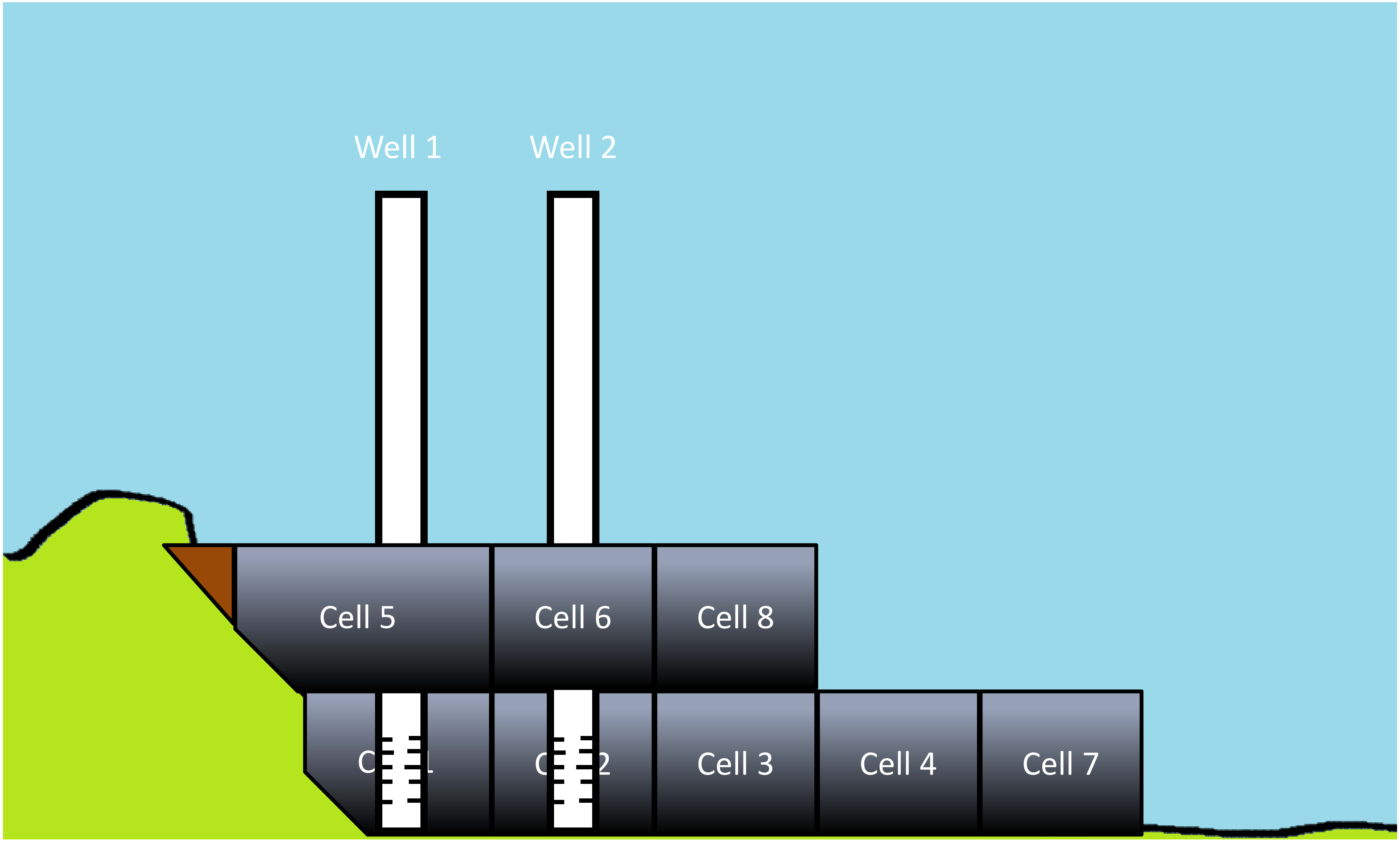
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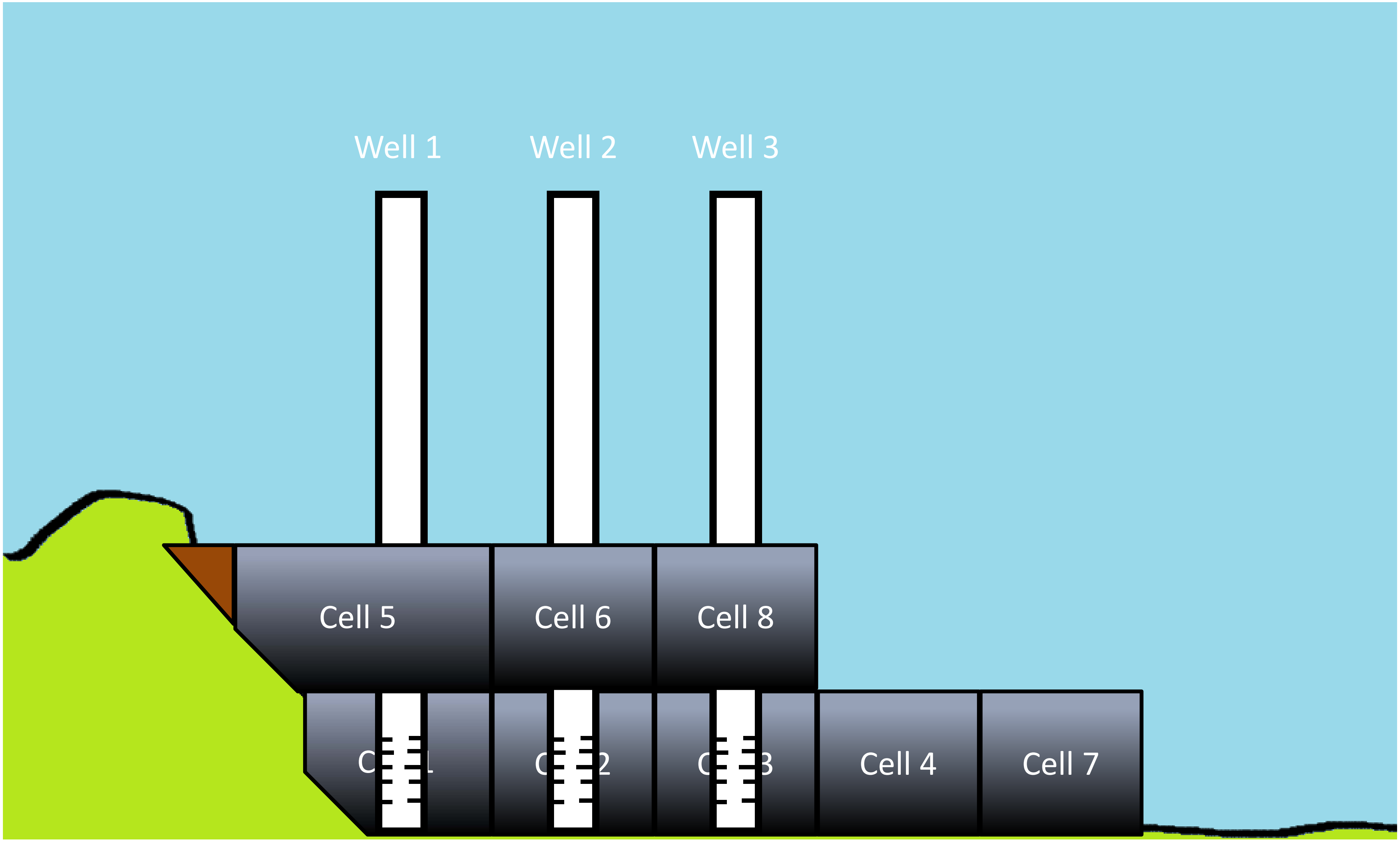
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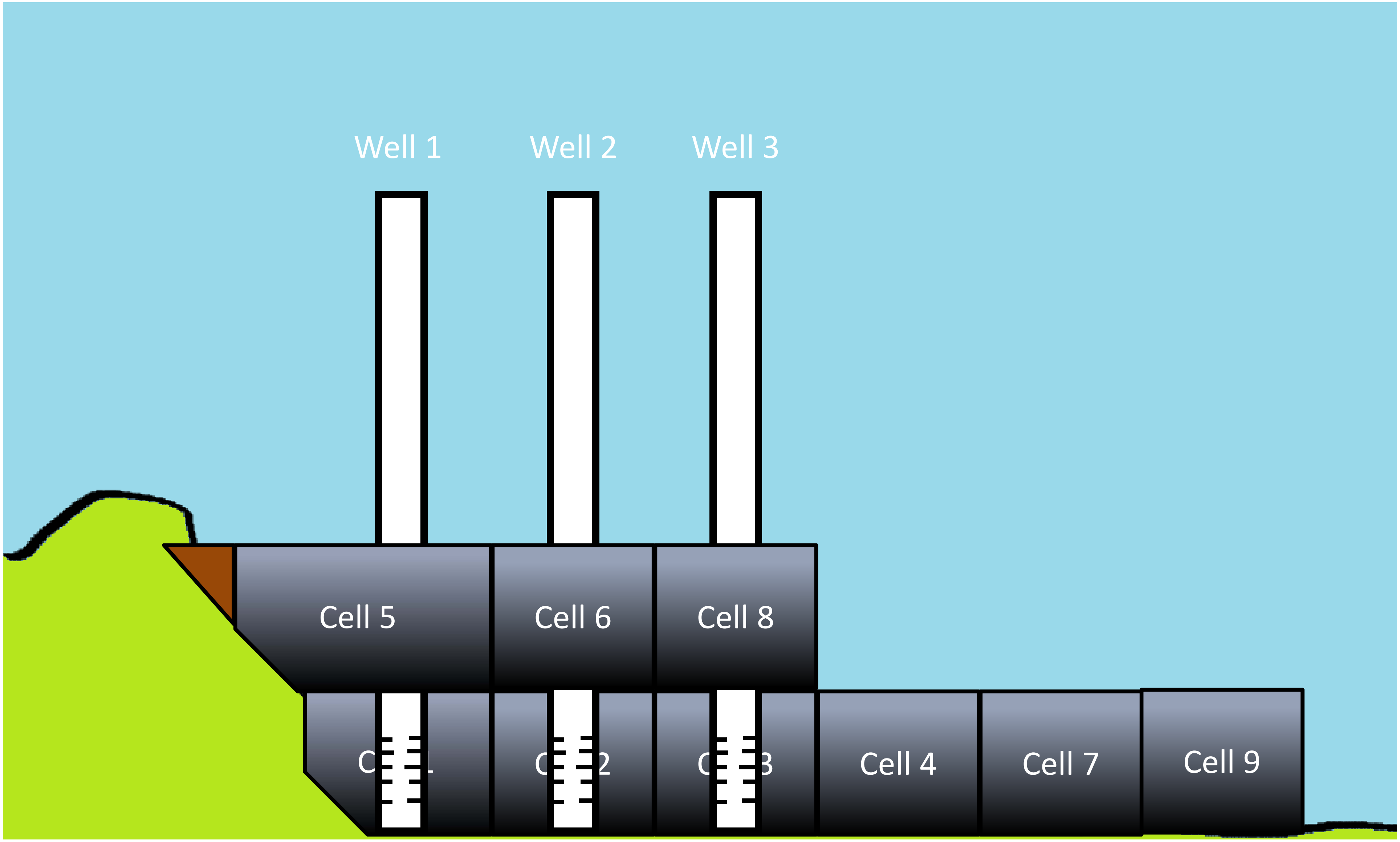
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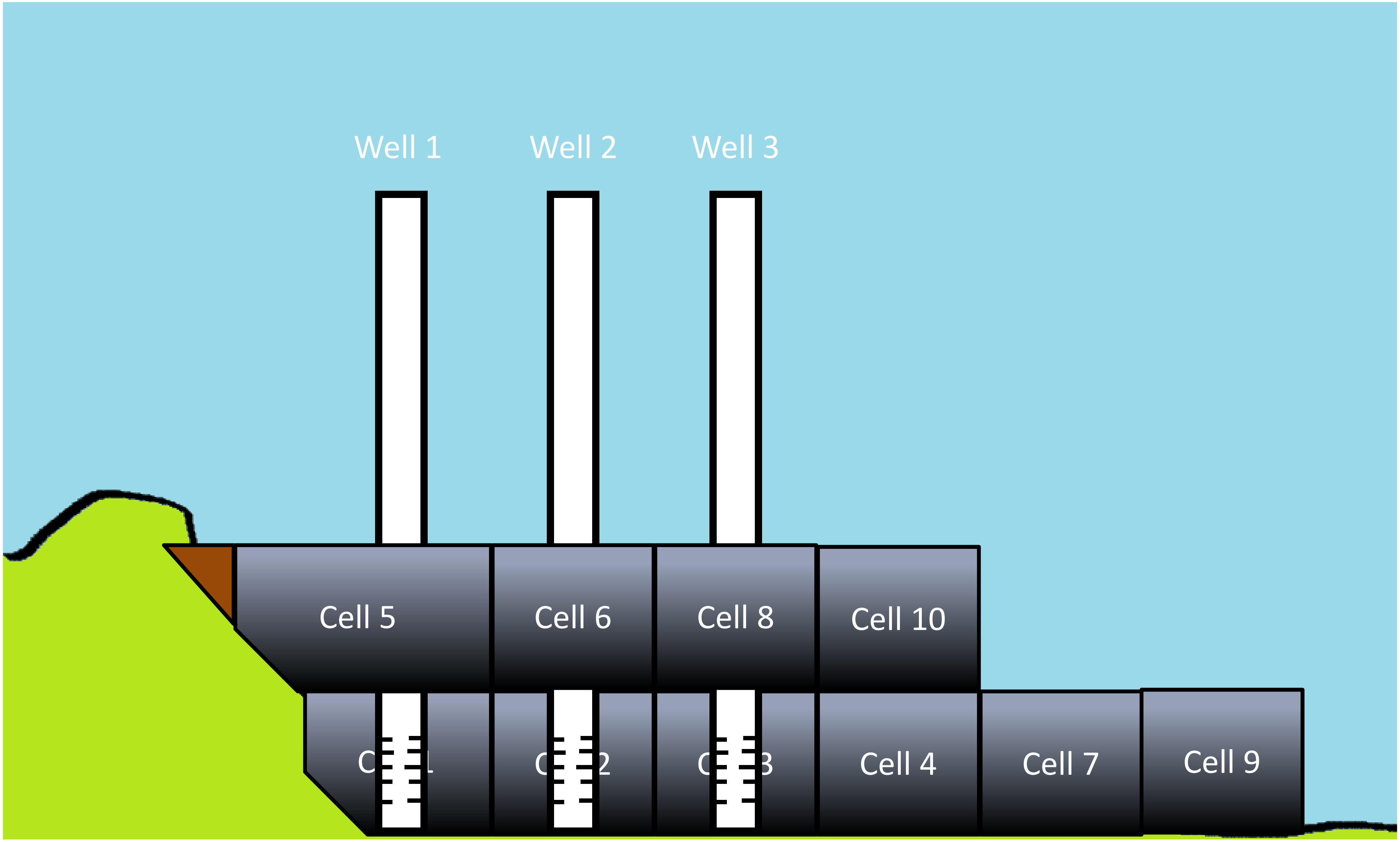
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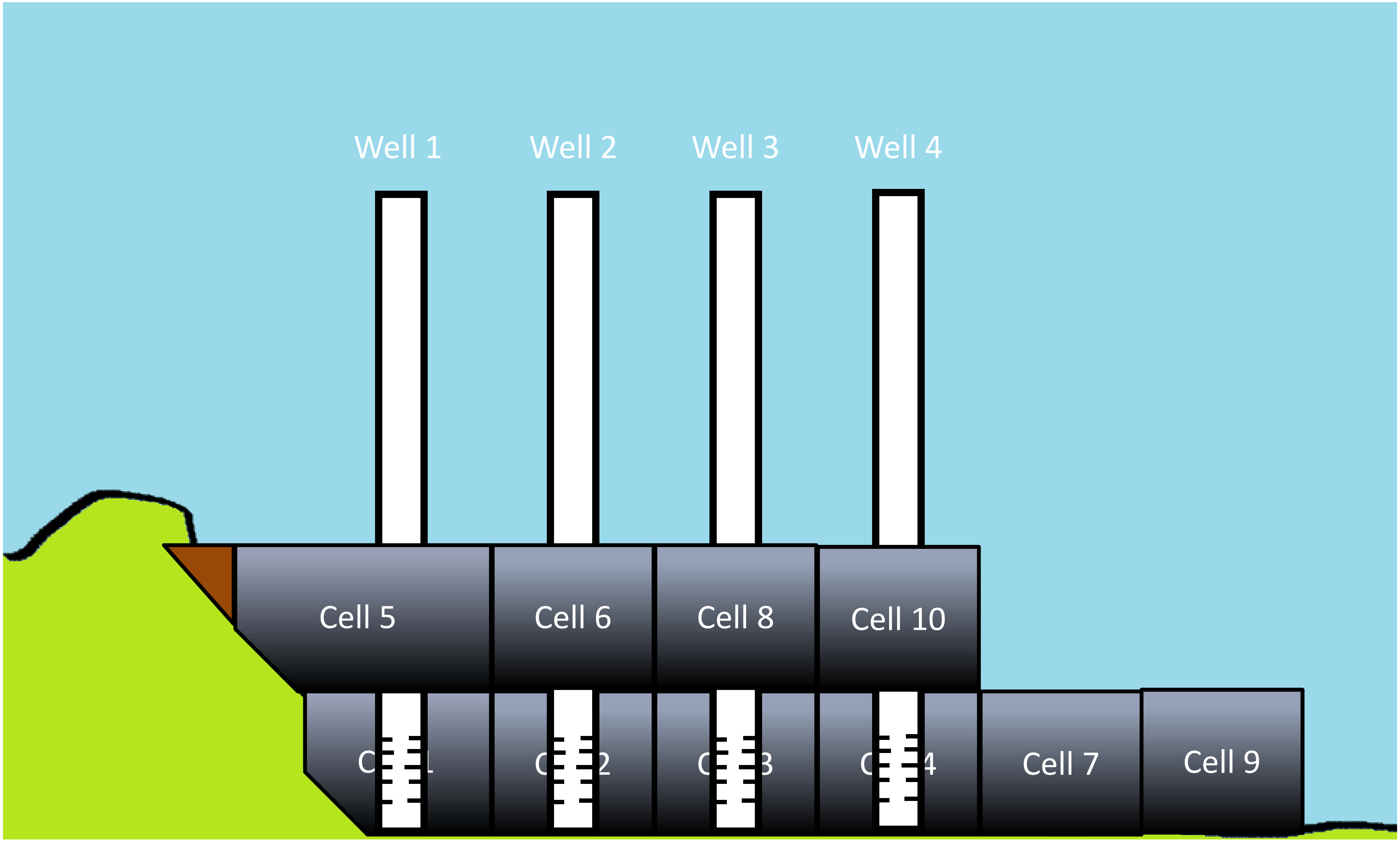
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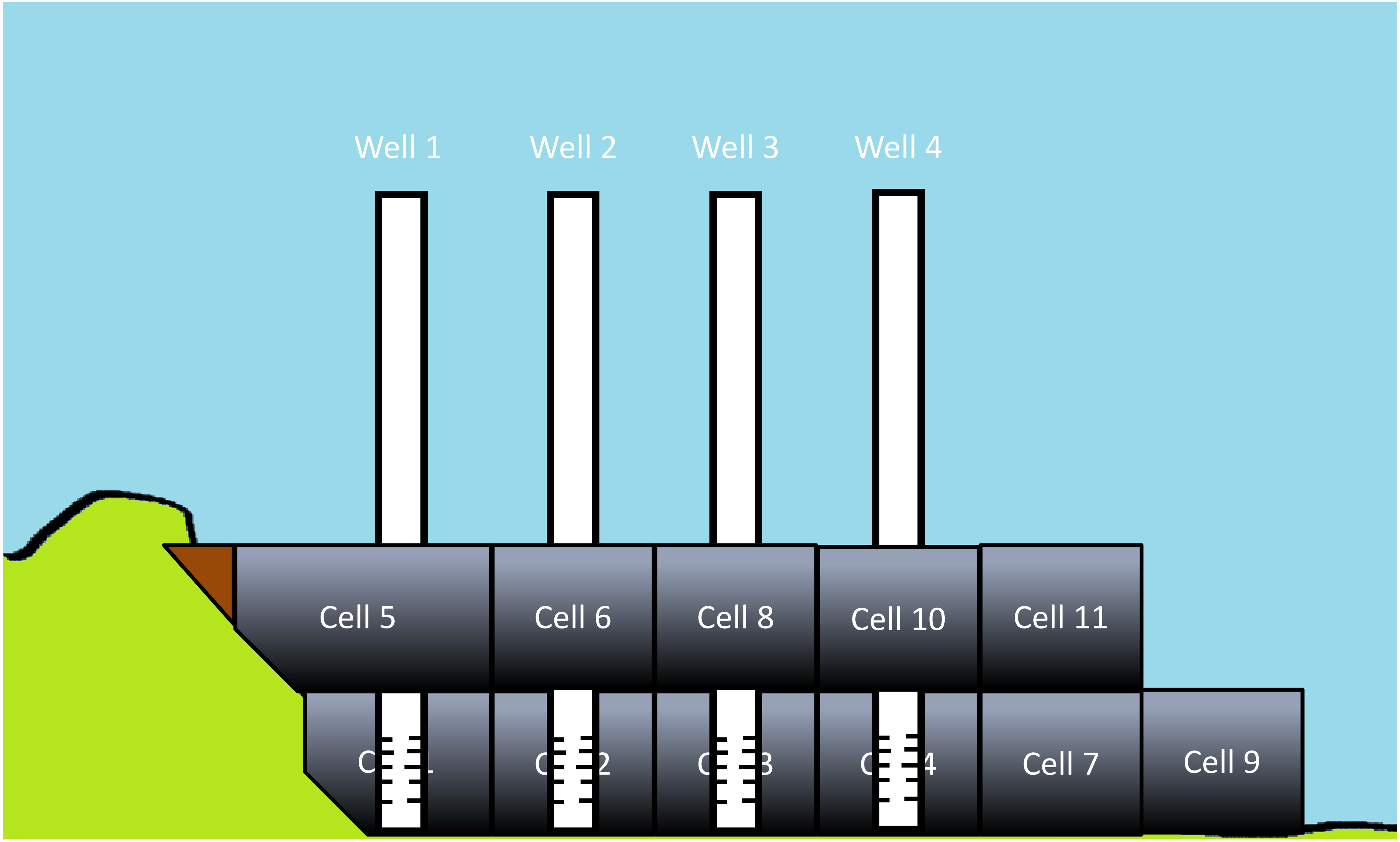
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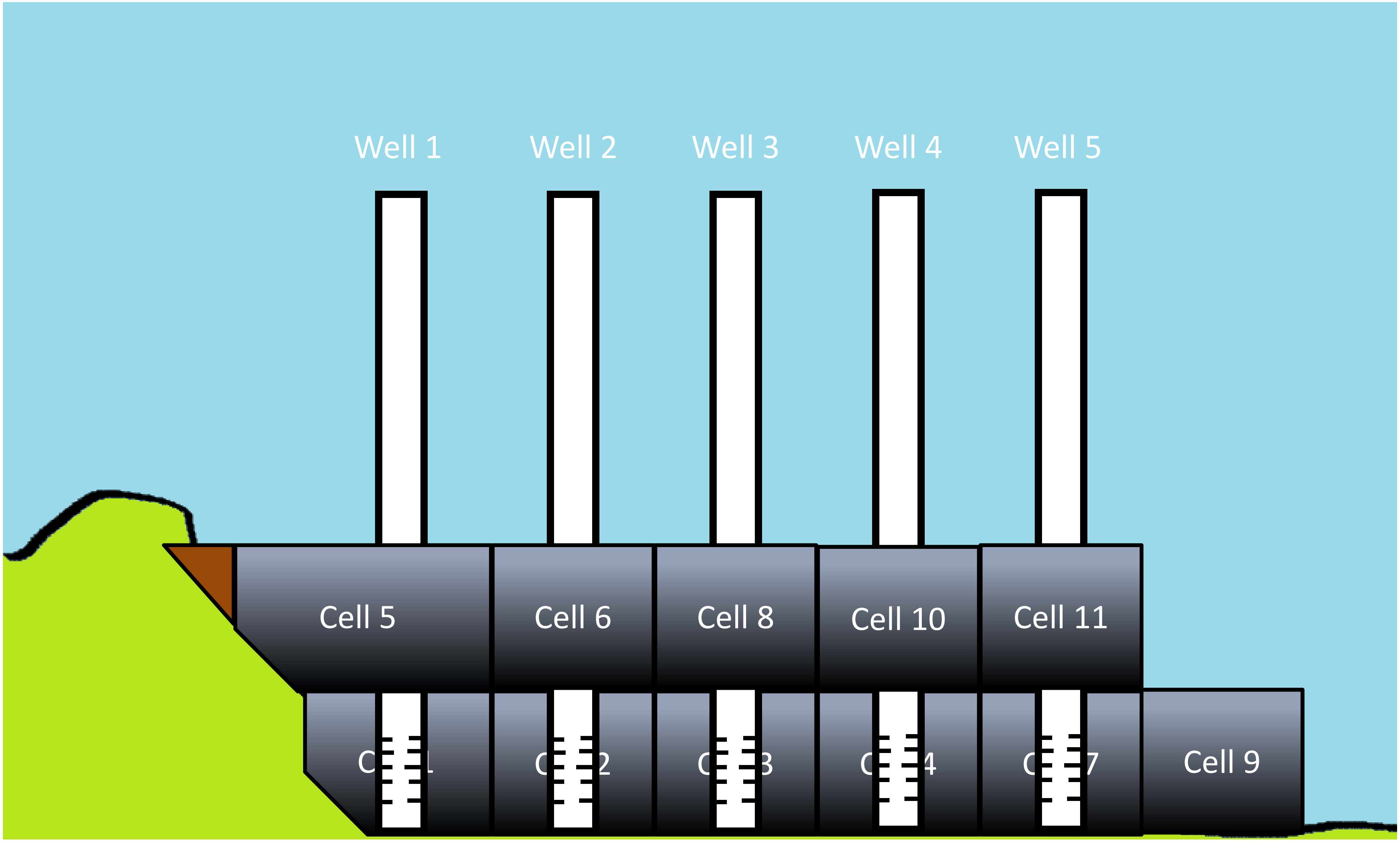
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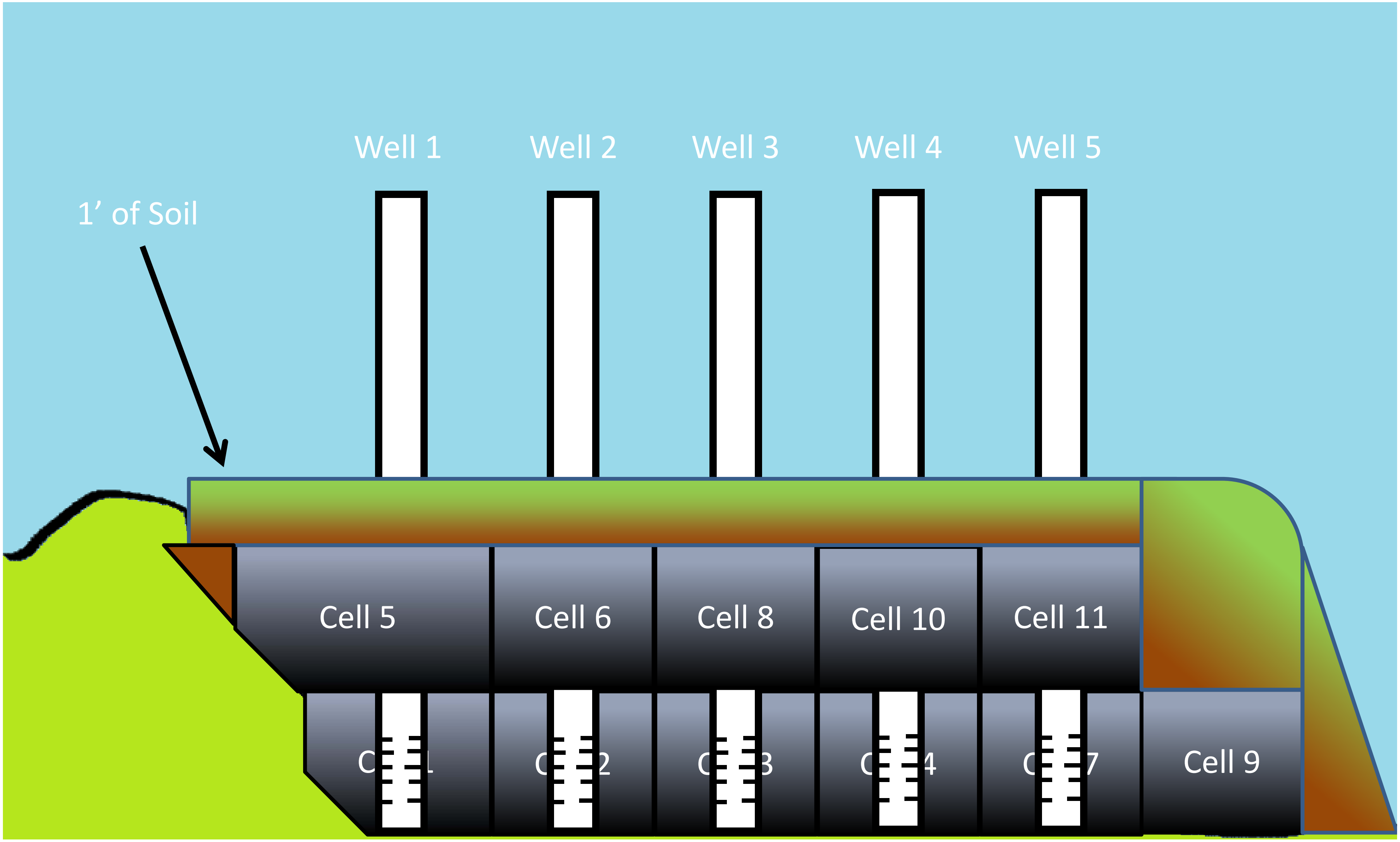

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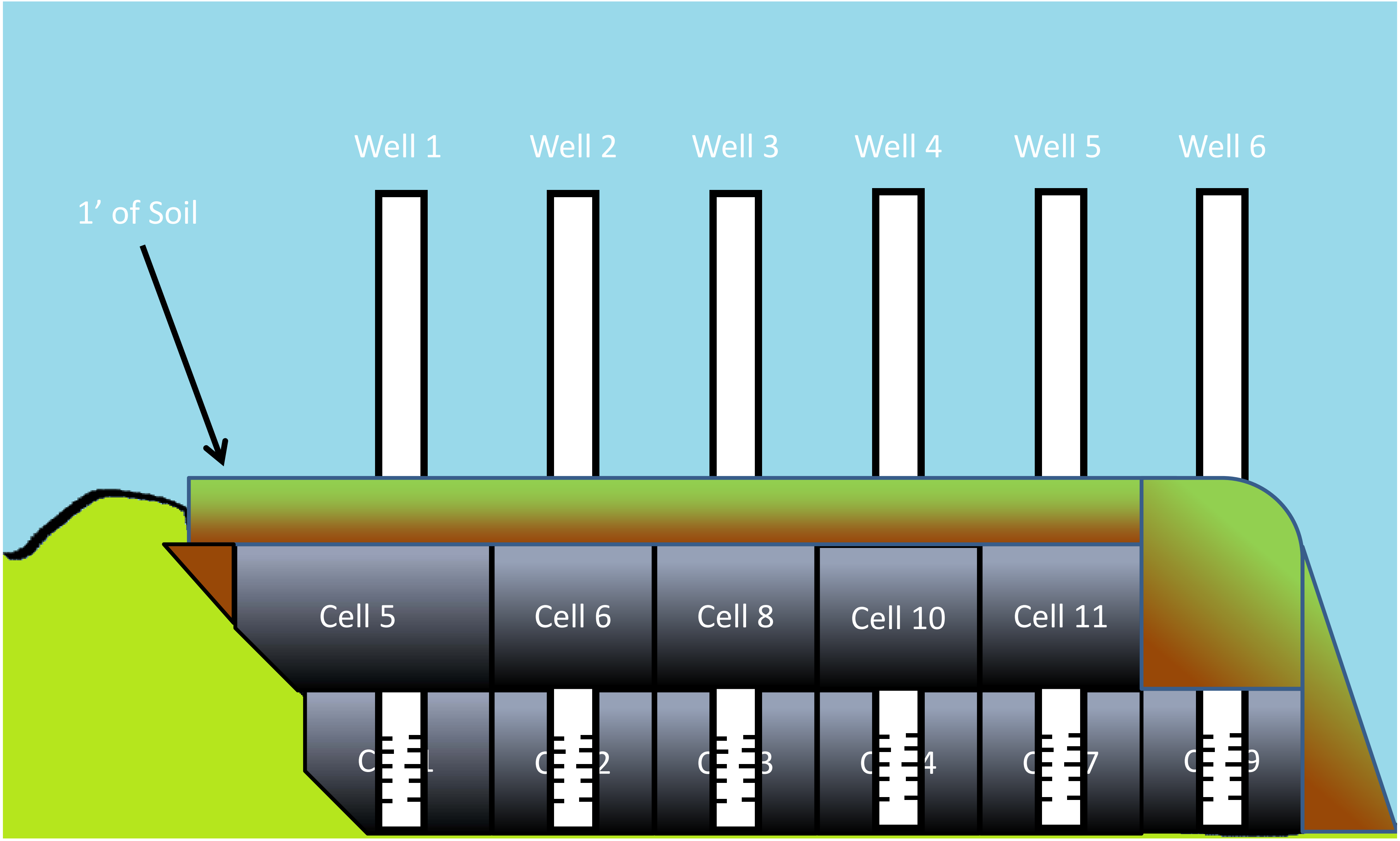
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Effect of decay rate on methane collection

- L_0 = 100 m^3/wet Mg
- Values for waste buried in first year.
- Overall collection efficiency varies with time, decay rate, landfill operation.

Landfill Gas Modeling

- Must be careful to use appropriate waste composition and quantity data
  - Mass of construction debris differs from a mass of food waste
  - Use multiple waste fractions
- Model results
  - Data should be presented as a range given uncertainty
  - Decreasing waste quantities will affect model predictions

U.S. EPA Defaults

- L_0 = 100 m^3 CH4/wet Mg (1 Mg = 1 metric ton = 1000 kg)
- k = 0.04 yr^{-1} in regions that receive >62.5 cm annual precipitation
- 0.02 in regions that receive <62.5 cm annual precipitation

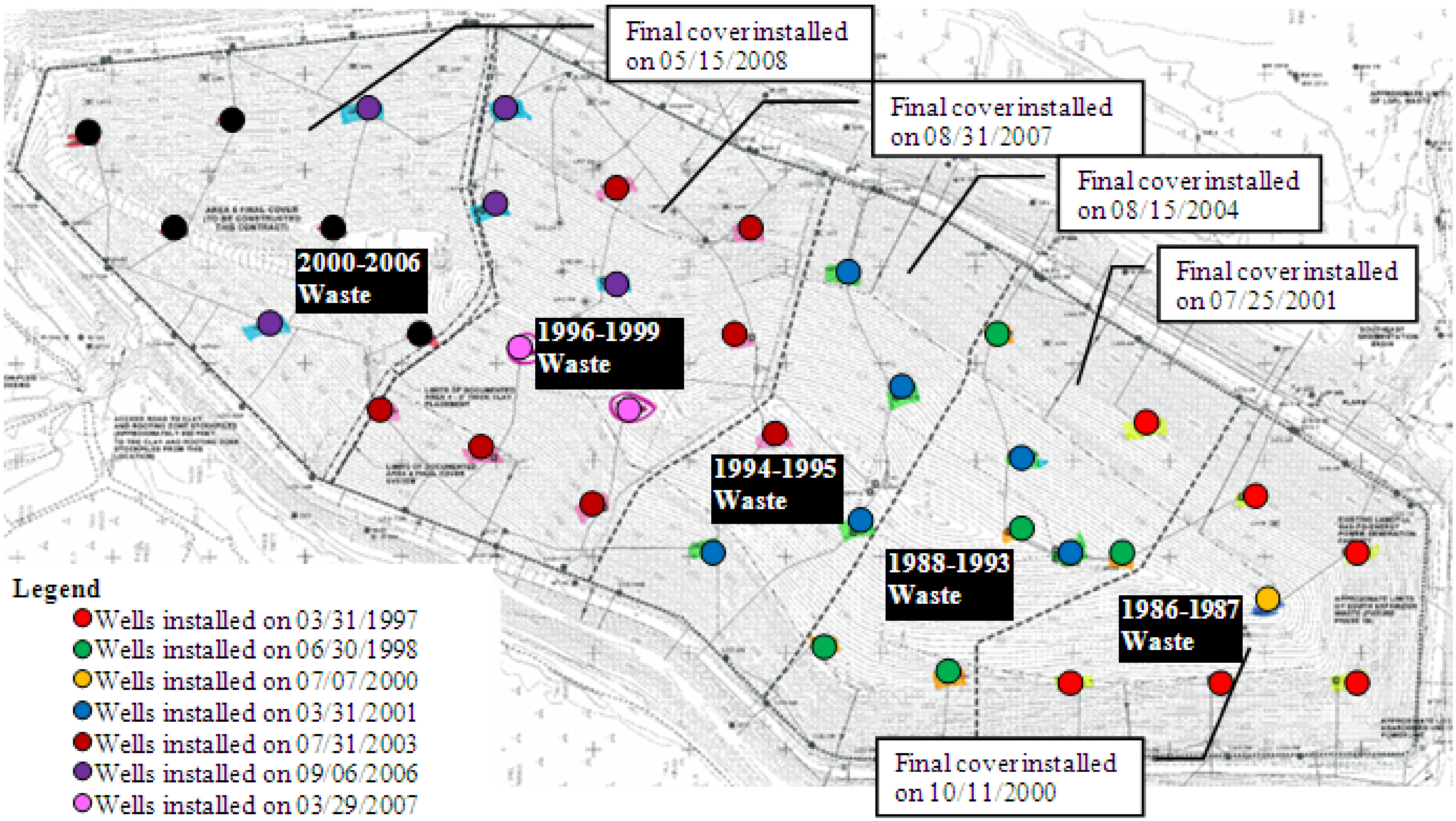
Landfill Gas Modeling

$$Q_n = k \cdot L_0 \cdot \sum_{i=0}^{n} \sum_{j=0.0}^{0.9} \frac{M_i}{10} \cdot e^{-k \cdot t_{i,j}}$$

- **Q_n** is annual methane generation for a specific year t (m^3 CH_4/yr);
- **k** is first order decay rate constant (1/yr)
- **L_0** is total methane potential (m^3 CH_4/ton of waste);
- **M_i** is the annual burial rate (wet tons)
- **t** is time after initial waste placement (yr);
- **j** is the deci-year time increment

Landfill Gas Emissions Model (LandGem)
http://www.epa.gov/ttn/catc/products.html#software

Location of Waste Disposal and Schedule of GCCS Installation at Landfill G



Legend
- Wells installed on 03/31/1997
- Wells installed on 06/30/1998
- Wells installed on 07/07/2000
- Wells installed on 03/31/2001
- Wells installed on 07/31/2003
- Wells installed on 09/06/2006
- Wells installed on 03/29/2007
- Wells installed on 11/14/2007

1986-1987 Waste — Years of waste burial

Final cover installed on 10/11/2000 — Date of final cover installation

Estimates of α_{ij} for Landfill G during Methane Collection (%)

Gas recovery period	Years of waste burial								
	1986-1995	1996-1999	2000-2004	2005	2006	2007	2008	2009	2010
Jan 05 – Sep 06	90	60	0	0	0	0	0	0	0
Oct 06 – Jun 07	90	75	40	0	0	0	0	0	0
Jul 07 – Nov 07	90	90	40	0	0	0	0	0	0
Dec 07 – Jun 08	90	90	75	75	75	0	0	0	0
Jul 08 – Aug 09	90	90	90	90	90	0	0	0	0
Sep 09 – Jun 10	90	90	90	90	90	20	0	0	0
Jul 10 – Dec 10	90	90	90	90	90	75	50	0	0

- Estimates are uncertain and require judgment, but changes with time cannot be ignored.

CH_4 generation potential (L_0) and corresponding optimized first order waste decay rate (k) for landfills

Landfill	Leachate recirculation	L_0 = 100
S	Y	0.12
G	Y	0.1
H	Y	0.15
T	Y	0.04
C1	N	0.17
P1	N	0.04
M	Y	0.17
Q	N	0.13
C2	N	0.15
P2	N	0.09
N	N	0.11

Landfills S, H, C1, M, Q, C2 have highest k; 3 recirculate and 3 do not

Landfill T has a low k and it recirculates.

Closure:
P1 - 2004
N - 2008

CH_4 generation potential (L_0) and corresponding optimized first order waste decay rate (*k*) for landfills

Landfill	Biosolids acceptance	$L_0 = 100$
S	Y	0.12
G	Y	0.1
H	Y	0.15
T	Y	0.04
C1	Y	0.17
P1	?	0.04
M	?	0.17
Q	Y	0.13
C2	Y	0.15
P2	Y	0.09
N	?	0.11

Landfills S, H, C1, M, Q, C2 have highest k; 5 accept biosolids.

Landfill T has a low k and accepts biosolids.

Closure:
P1 - 2004
N - 2008

Concluding Comments

- Gas production, leachate composition and solids decomposition are interrelated
- Solids decomposition will never reach 100%
- Gas production and gas collection are complex and must consider landfill gas system implementation

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  - Delaware Solid Waste Authority
  - Yolo County, CA
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  - CH2MHill
  - Geosyntec Consultants
- Regulatory Agencies
  - U.S. EPA
  - New York Department of Environmental Conservation
  - Wisconsin Department of Natural Resources
- Industry Associations
  - Environmental Research and Education Foundation
  - National Council for Air and Stream Improvement

Organic Composition of Residential Refuse (% Dry Wt.)

	News print	Copy Paper	OCC	Coated Paper	Branches	Grass	Leaves	Food Waste
Cellulose	44-48	58-65	57.3	35-42	27-40	26.5	15.3	18-33; 55 (incl. starch)
Hemi-cellulose	16.5-18	12.5	9.9	7.4-11.9	15-19	10.2	10.5	1; 7.2
Lignin	22-25	1.0	20.8	3.3-19.6	22-36	28.4	43.8	1.5; 11.4
Volatile solids	96-98	77-88	92.2	56-74	96-99	85	90.2	93.8

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